SOURCE IDENTIFICATION OF PESTICIDE POLLUTION AND DETERMINATION OF NORMAL BACKGROUND CONCENTRATIONS OF METALS IN YEŞİLIRMAK RIVER BASIN

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ABSTRACT

SOURCE IDENTIFICATION OF PESTICIDE POLLUTION AND DETERMINATION OF NORMAL BACKGROUND CONCENTRATIONS OF METALS IN YEŞİLIRMAK RIVER BASIN

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Surface waters are one of the most vulnerable environmental compartment to the pollution pressures arising from numerous point and nonpoint sources. In this thesis, pesticide pollution and metal pollution as being two major concerns of the Yeşilırmak River Basin were addressed by pursuing target-oriented analysis and comprehensive assessment approaches. The main objective of this thesis is to establish the basin-spesific normal background concentrations (NBCs) and environmental quality standards (EQSs) for the metals and to determine target-specific agricultural sources of the pesticides in the Yeşilırmak River Basin. In this context, the basin-specific NBCs and EQSs were determined for 26 metals and metalloids. As a result of these analysis and assessments, the basin-specific EQSs were derived as 47.8 µg/L, 13.2 µg/L, and 98.6 µg/L for Al, Cu, and Fe, respectively. Within the scope of the agricultural source identification of the pesticide pollution, the insecticide, herbicide, and fungicide spraying schedules of each crop type raised in the districts of the river basin were analyzed by focusing on district-specific assessments. Furthermore, the spatial distribution pathway and the temporal occurrence trend of the pesticides across the river basin were identified to establish the basin-wide profile of the pesticide pollution. Precipitation regime, district altitude, mobility, and persistence of pesticides, which are the major factors affecting pesticide occurrences in the river, were also analyzed for the well-supported source identification of the pesticide pollution. This thesis offers a goal-oriented baseline to fulfill the functional implementations of the river basin management strategies that are adjusted to site-specific conditions.

Keywords: Pesticide Source Identification, Target-Specific, Metal Pollution, Background Concentration

ÖZ

YEŞİLIRMAK HAVZASI'NDA PESTİSİT KİRLİLİĞİ KAYNAK BELİRLEME ÇALIŞMASI VE METALLER İÇİN ARKAPLAN KONSANTRASYONLARININ BELİRLENMESİ

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Yüzey suları, birçok noktasal ve yayılı kirleticiden kaynaklanan kirlilik baskılarına karşı en savunmasız alanlardan biridir. Bu tezde, Yeşilırmak Nehir Havzası'nın iki temel sorunu olan pestisit kirliliği ve metal kirliliği, hedef odaklı analizler ve kapsamlı değerlendirme yaklaşımları takip edilerek ele alınmıştır. Bu tezin temel amacı, metaller için havza bazlı normal arkaplan konsantrasyonlarını ve çevresel kalite standartlarını oluşturmak, ve havzada gözlemlenen pestisitlerin hedefe özel tarımsal kaynaklarını belirlemektir. Bu bağlamda, 26 metal ve metaloit için havza bazlı normal arkaplan konsantrasyonları ve çevresel kalite standartları belirlenmiştir. Bu analiz ve değerlendirmeler sonucunda havza bazlı çevresel kalite standartları Al, Cu ve Fe için sırasıyla 47,8 µg/L, 13,2 µg/L ve 98,6 µg/L olarak hesaplanmıştır. Pestisit kirliliğinin tarımsal kaynak tespiti kapsamında, nehir havzası ilçelerinde yetiştirilen her bir ürün türüne ait insektisit, herbisit ve fungisit ilaçlama programları ilçe bazlı değerlendirmeler doğrultusunda analiz edilmiştir. Buna ek olarak, pestisit kirliliğinin havza genelindeki profilini tespit etmek amacıyla pestisitlerin nehir havzası boyunca mekansal dağılımı ve zamansal oluşum trendleri belirlenmiştir. Pestisit kirliliğinin güvenilir kaynak tespiti için nehirdeki pestisit oluşumunu etkileyen en önemli faktörler olan yağış rejimi, ilçe rakımı, pestisit hareketliliği ve kalıcığı da analiz edilmiştir. Bu tez çalışması, sahaya özgü koşullara göre adapte edilmiş nehir havzası yönetim stratejilerinin işlevsel uygulamalarını hayata geçirmek için hedef odaklı bir temel sunmaktadır.

Anahtar Kelimeler: Pestisit Kaynak Belirleme, Hedefe Özgü, Metal Kirliliği, Arkaplan Konsantrasyonu

To my family

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TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

CHAPTER 1

INTRODUCTION

Severely increasing pressures of metals and pesticides on the freshwater environment have raised great concern and become today's most urgent environmental issue regarding the water quality of freshwater bodies around the world. The widespread implementations of agricultural activities and the constantly growing industrilization are mainly responsible for the deterioration of the freshwater environment in parallel with aquatic life and human health by contributing to metal and pesticide pollution. Especially, river bodies are considerably exposed to these pollutants due to wastewater discharges of industries and diffuse loads from agricultural land use via mechanisms such as surface runoff, erosion, spray drift and atmospheric deposition. For the mitigation and elimination of these pollutants, their occurrence, sources and distribution in river bodies should be paid particular attention by addressing site-specific analysis and assessment approach, which offer viable, goal-oriented, and site-adjusted solutions. In this respect, this thesis has focused on establishing basin-specific normal background concentrations (NBCs) and environmental quality standards (EQSs) for the metals, and target-specific agricultural source identification of pesticides observed in the Yeşilırmak River Basin. The present study was carried out as an integral part of the Project entitled "Management of Point and Diffuse Pollution Sources in the Yeşilırmak River Basin" supported by TUBITAK with the project code of 115Y013. The Project was run by the METU Department of Environmental Engineering, in cooperation with the Munzur University and TUBITAK Marmara Research Center (MAM) Environment and Cleaner Production Institute.

In the following sections, firstly, a general description of the Yeşilırmak River Basin is provided, and then the objective and the scope of the thesis are presented.

1.1 Study Area

The Yeşilırmak River Basin is located in the northern part of Anatolia by occupying approximately 38,000 km^2 area. Among the 25 river basins of Turkey, the Yeşilırmak River Basin is the third largest river basin regarding the surface area. The Yeşilırmak River, which has a 519 km length, is originated from the Köse Mountains and flows into the Black Sea. The Yeşilırmak River Basin embodies 11 provinces, which comprise Gümüşhane, Giresun, Sivas, Tokat, Amasya, Samsun, Çorum, Yozgat, Bayburt, Ordu and Erzincan. Among these provinces, more than 50% of the area of Tokat, Amasya, and Samsun provinces is located within the boundaries of the river basin. The river basin embodies the different climatic conditions, which encompass the impacts of the Central Black Sea climate, Western Black Sea climate, and Central Anatolia climate (TUBITAK MAM, 2010). The high diversity of the climatic conditions brings about the high diversity of agricultural crops cultivated within the boundaries of the river basin. In total, 179 different types of agricultural crops that have economic value are raised within the boundaries of the basin (TurkStat, 2020). The river basin also incorporates various types of industrial activities, which involve the manufacture of metal, food, textile, machinery, and plastic products (TUBITAK MAM, 2010). In this respect, the industrial and agricultural activities in the river basin are considerably intense and variable. Therefore, the industrial and agricultural activities performed in the Yeşilırmak River Basin have a high potential to contribute to the pesticide and metal pollution in the river body.

1.2 Objective of the Thesis

This thesis aims to provide an insight into the site-specific problems associated with the metal pollution and pesticide pollution in the Yeşilırmak River Basin by focusing on target-specific analysis and assessment of the polluted site. In this regard, the main objective of this thesis is to derive the basin-specific NBCs and to establish the basin-specific EQSs for the metals and, to identify target-specific agricultural sources of pesticide pollution in the Yeşilırmak River Basin. Furthermore, this thesis aims to determine spatial and temporal occurrence trends of the pesticide pollution across the river basin by individually assessing the impacts of precipitation, district altitude, mobility of the pesticides and, water and soil half-lives of the pesticides in the river basin.

1.3 Scope and Outline of the Thesis

The scope of this thesis is presented below:

- The derivation of basin-specific NBCs for the metals and metalloids in the Yeşilırmak River Basin
    - The pre-treatment and compilation of metal concentration data
    - The implementation of outlier detection test
    - The employment of data treatment for below-limit of detection values (below-LODs) with three different approaches
    - The implementation of low percentile analysis
- The establishment of basin-specific EQSs for the metals and metalloids in the Yeşilırmak River Basin
- The identification of district-specific agricultural sources of the pesticide pollution within the boundaries of the Yeşilırmak River Basin
    - The data collection and compilation regarding the information on the type, spraying frequency, and spraying timing of the agrochemicals against the district-specific and crop-specific pests by personally contacting the agricultural engineers of the District Directorates of Agriculture and Forestry
    - The preparation of comprehensive inventories, which encompass the typical agricultural practices and crop-specific insecticide, herbicide and fungicide spraying schedules for each district where sampling stations are located

  - The identification of the dominant crops grown in each district of the river basin by calculating areal shares of each crop at district scale and basin scale
  - The analysis and determination of the type and the pollution level of the pesticides that exceeded their annual average EQS (AA-EQS) and maximum allowable concentration EQS (MAC-EQS) values at the sampling stations of each district
  - The analysis and assessment of the temporal correlations between the agricultural activities and the pesticide occurrences observed at the sampling stations of each district
- The determination of spatial distribution pattern of the pesticide pollution across the Yeşilırmak River Basin
  - The analysis and assessment of the relation between the spatial distribution of the agricultural areas and the pesticide occurrence pathway across the river basin
  - The analysis and assessment of the impact of water and soil half-lives of the pesticides on their detection frequencies across the river basin
  - The analysis and assessment of the relation between the mobility of the pesticides and their spatial distribution across the river basin
  - The analysis and assessment of the impact of district altitude on the diversity of the pesticide types observed at the sampling stations of each district of the river basin
- The determination of temporal occurrence trend of the pesticide pollution across the Yeşilırmak River Basin
  - The analysis and assessment of the relation between the precipitation trend and temporal occurrence trend of the pesticides in the river basin

Within the context of this thesis, in Chapter 1 (Introduction), general information about the Yeşilırmak River Basin, and the overall objective and scope of the thesis are given to provide a general overview of the thesis.

In Chapter 2, *Establishment of Normal Background Concentrations and Environmental Quality Standards for Metals in Yeşilırmak River Basin* is studied and presented by pursuing a stepwise procedure (Introduction, Background, Methodology, Results and Discussion, Conclusion and Recommendations). Within the scope of Section 2.1 (Introduction), the importance of the establishment of river basin specific NBCs and EQSs were explained by providing the regulatory status of river basin specific EQS derivation both in Turkey and the European Union (EU). In addition, the objective and scope of the study are described in this section. In Section 2.2 (Background), the general information about metal pollution in the freshwater environment is provided. Furthermore, fate and typical sources of metals and metalloids in the environment, the use of "normal" and "natural" terms for background concentration concept in literature and literature review on background concentration assessment techniques are presented within the scope of Section 2.2. In Section 2.3 (Methodology), the techniques and approaches that are addressed to derive and establish basin-specific NBCs and EQSs for the metals in the Yeşilırmak River Basin are explained in detail. In this section, data selection and compilation, outlier detection test: Adjusted Tukey's Method, below-LOD treatment by introducing three different approaches, derivation of basin-specific NBCs by the low percentile analysis technique and the calculation method of the basin-specific EQSs are described and explained by presenting each of these steps in individual subsections. In Section 2.4, the results of data selection and compilation, outlier detection test, low percentile analysis results under the three different below-LOD treatment approaches, the derived basin-specific NBCs and the calculated basin-specific EQSs for each metal and metalloid were presented and discussed, comprehensively. In Section 2.5 (Conclusion and Recommendations), the overall importance, benefits and outcomes of the study are summarized and recommendations for future research are proposed within the scope of Chapter 2.

In Chapter 3, *Agricultural Source Identification of Pesticide Pollution in Yeşilırmak River Basin* is studied and presented within the context of five main sections (Introduction, Background, Methodology, Results and Discussion, Conclusion and

Recommendations). In Section 3.1 (Introduction), the importance of target-specific agricultural source identification of pesticide pollution, and the relation between pesticide use and agricultural activities are explained by providing regulatory scope and status of plant protection products in Turkey and EU. In addition, detailed objective and scope of the study are given in this section. In Section 3.2 (Background), the impact of crop types and locality of farmlands on pesticide uses, fate of pesticides from agricultural fields to the freshwater environment and impact of physicochemical characteristics of pesticides on pesticide occurrences in the freshwater environment are individually explained and presented. In Section 3.3 (Methodology), the approaches that are followed in the data compilation and analysis, and in the selection of the basin-specific pesticides are presented. Moreover, the procedures that are addressed for the assessment of the spatial distribution of the pesticide pollution across the river basin, the assessment of the temporal occurrence trend of the pesticide pollution across the river basin and district-specific identification of the agricultural sources for the pesticides in the river basin are described and presented within the scope of Section 3.3 (Methodology). In Section 3.4 (Results and Discussion), the results of data analysis, spatial distribution pattern and temporal occurrence trend of pesticides and district-specific source identification of pesticides were provided. In Section 3.5 (Conclusion and Recommendations), the importance and summary of the study and suggestions for future researches are presented within the scope of Chapter 3.

In Chapter 4 (Concluding Remarks), the overall summary of the studies that are performed within the scope of both in Chapter 2 and Chapter 3 are explained and presented to provide a clear picture and general perspective about the overall fulfillments of the thesis.

CHAPTER 2

ESTABLISHMENT OF NORMAL BACKGROUND CONCENTRATIONS AND ENVIRONMENTAL QUALITY STANDARDS FOR METALS IN YEŞİLIRMAK RIVER BASIN

2.1 Introduction

Surface water metal contamination has become a huge environmental issue with increasing global industrialization and urbanization. With the contribution of point and non-point pollution sources, metals present in freshwater environments reach high levels, which pose a severe threat both for aquatic life and human health. On the other hand, metals play a vital role by participating ecological cycle and by being a substantial part of biological systems since they can be essential nutrient sources for some of the living organisms at certain existence levels. The balance between the degree of benefit and disruption effects of metals changes depending on regional characteristics of freshwater environment like geology, topography, type of soil, and climate of a specific field. Therefore, the natural contributions of metals to freshwater contamination should be determined by taking into consideration regional natural characteristics of the freshwater environment in order to figure out if existing concentration levels are part of the anthropogenic inputs or natural origins. This can be achieved by the establishment of basin-specific NBCs. On the basis of the EU Water Framework Directive (WFD) (2000/60/EC) and the Environmental Quality Standards Directive (EQSD) (2008/105/EC), the establishment of basin-specific EQSs is substantial responsibility of the EU member states in order to reach "good status" for water quality. For the determination of basin-specific EQSs, one of the fundamental requirements is the derivation of basin-specific NBCs. The WFD (2000/60/EC) also requires the EU member states to prepare and implement river basin management plans (RBMPs). For the development and implementation of environmental management strategies, the extent of contamination levels and their sources should be determined by establishing river basin specific EQS values. For the development of target-specific and effective remediation strategies, the derivation of basin-specific EQSs and background concentrations gains critical importance as a part of the implementation of RBMPs. Moreover, a set of discharge limits can be accomplished in the light of background concentration information. All in all, the determination of the basin-specific EQSs and NBCs is one of the key steps for the implementation of well-developed water quality management strategies. For the fulfillment of these goals, in this study, basin-specific NBCs and basin-specific EQSs were established for the Yeşilırmak River Basin. Within the context of this study, pre-treatment and compilation of data, implementation of outlier test by Adjusted Tukey's Method, below-LOD treatment by introducing three different approaches and employment of low percentile analysis were conducted by using the concentration data of each metals and metalloids observed in the Yeşilırmak River Basin.

2.2 Background

2.2.1 Metals and Metalloids in the Environment

One of the most abundant chemical groups present in the natural environment is "metals and metalloids", which naturally exist in the crust of the Earth. Metals are released and spread through the atmosphere, soil, freshwater, and other environmental compartments by the erosion of rocks, weathering, runoff from land, and rain events. Besides natural sources, a considerable fraction of metals has been introduced to the freshwater environment by anthropogenic activities with increasing industrialization and urbanization. Primary anthropogenic sources of metals are mining activities, inputs, and runoff from iron-steel plants, smelters, and urban wastewater treatment plant effluents (Rainbow, 2018). All these different factors affect the transportation pathway of metals by creating complex input-output relations between different environmental compartments. Since metal background concentration in a river basin depends on a variety of factors like geology, topography, precipitation regime, and climate of the target region, determination of metal background values is quite complicated and requires a detailed study (Mast, Verplanck, Wright, & Bove, 2007).

According to the Regulation on Surface Water Quality (Official Gazette No:29797, 2016), basin-specific background concentrations are required to be determined for 13 metals and metalloids, which are Al, Sb, As, Cu, Zn, B, Fe, Sn, Hg, Co, Cr, Ti and V. Within the context of this study, in addition to these 13 metals, evaluation of Ba, Be, Cd, Ni, Pb, Hg, Si, Ti, CN^-, Mn, Se, S^{-2}, Ca and Mg was also performed for the purpose of background concentration determination. In total, the assessment of 26 metals and metalloids which are observed during the monitoring studies in the Yeşilırmak River Basin were conducted with regard to the WFD (2000/60/EC), EQS Directive (2008/105/EC) and Regulation on Surface Water Quality (Official Gazette No:29797, 2016).

2.2.2 "Normal" Background Concentration (NBC) Concept

In literature, "normal" background concentration term is interchangeably used with the replacement of "ambient" or "usual" background concentration terms. All these three terms (normal, usual, and ambient) define background concentration that is contributed by both diffuse anthropogenic sources and the natural environment (Peters, Merrington, & Crane, 2012; International Organization for Standardization (ISO), 2005).

Another expression commonly used to describe background concentration is "natural" which implies different meanings than "normal, ambient or usual" background. Natural background concentration term mainly refers to the concentration of a chemical compound which is entirely originated from the natural environment. For the estimation of natural background, not only major point sources but also anthropogenic sources like atmospheric depositions, diffuse releases, and impact of historical contributions should not exist within the data obtained from the river basin and vicinity of the river basin. However, in the Yeşilırmak River Basin, it is unlikely to eliminate entire contributions of anthropogenic sources from the data obtained by monitoring studies, especially when the existence of diffuse anthropogenic sources and historical anthropogenic inputs in the river basin are taken into consideration for the assessment of background concentration. Moreover, it is relatively difficult to make a clear distinction between these diffuse anthropogenic fractions and natural fractions of metal contribution to the river basin. According to Galuzka (2007), results of all chemical analysis obtained from the environments regarded as "pristine" comprise contributions both from natural sources and human influences. Moreover, the European Commission (2011) stated that it is almost impossible to remove entirely the impact of human exposures on background levels determined; thus, any background concentration value identified with the term "natural" is actually "ambient or normal" background value. In other words, even if major anthropogenic inputs are removed from the data, a low fraction of human impact will inevitably exist in the calculated background concentrations (Zgłobicki, Lata, Plak, & Reszka, 2011). Hence, in this study, it was preferred to perform an investigation for the determination of "normal background concentration" which represents contributions from both minor diffuse anthropogenic inputs (like atmospheric depositions and historical anthropogenic releases) and natural sources rather than "natural background concentration" in order to follow precise and realistic approach during the data analysis. As it is explained, major anthropogenic inputs can be eliminated from datasets, but these minor diffuse effects which are entirely integrated with natural contributions can only be minimized at a certain level. By following a realistic and reliable point of view, in this study, low-level fractions generated by diffuse anthropogenic sources were also accepted as a part of datasets and aimed to be minimized rather than complete exclusion in order to eliminate uncertainties resulting from the inevitable effect of diffuse anthropogenic contributions.

2.2.3 Background Concentration Assessment Techniques

Within the context of environmental quality researches, various approaches have been introduced to the literature depending on the features of available data and characteristics of the study area for the determination of background concentration. Qualitative investigations and quantitative implementations (like modeling and statistical analysis) are two main approaches that are proposed for the determination of background concentration.

Runnells, Shepherd, & Angino (1992) stated that the qualitative approach is one of the most simple and useful ways of background assessment. This approach is based on a comparison between currently existing data and historical water quality data, which represents the status of an undisturbed natural environment (Runnells, Shepherd, & Angino, 1992). On the other hand, knowledge obtained from historical metal concentration data, which represents the natural background, goes under an alteration over time with geologic and climatic changes. Even though concentration values obtained from historical observations give purely natural results of past times, these values may not represent the current pristine status of the target environment. Therefore, background concentration assessment based on a comparison of the measurement results from current and past datasets may not reflect correct background values.

Regarding quantitative approaches, modeling and statistical techniques are widely implemented procedures for the determination of background values. Carrasco-Cantos, Vadillo-Pérez, & Jiménez-Gavilán (2013) emphasized that hydrochemical modeling enables to investigate variations of water quality and the general transportation mechanism of chemicals. However, hydrochemical modeling studies require comprehensive information, including detailed data about the geological and hydrological characteristics of the study area. Moreover, the implementation of these modeling techniques is only applicable for small environments with a high number of parameters observed through long measurement periods (Urresti-Estala, Carrasco-Cantos, Vadillo-Pérez, & Jiménez-Gavilán, 2013). As a consequence, when hydrodynamic properties, geology, complex transportation mechanism, biological and chemical interactions of metals with the contact environment are taken into account, the accuracy of modelling requires quite an extensive and detailed available database and also expert knowledge from different field of studies.

Compared to qualitative methods and modelling studies, statistical techniques have emerged as a reliable approach for determining background concentration. Ander et al. (2013) suggested that statistical methods provide to obtain robust background concentration results by reducing the impacts of anthropogenic point pressures on datasets. Implementation of analysis with a minimum number of assumptions is one the most substantial feature of a methodology to be followed in order to conduct accurate background analysis. With the advantages of relatively low subjectivity and strong assessment, statistical methods are accepted as a precursor in many studies performed recently in literature for background concentration determination purpose (Urresti-Estala, Carrasco-Cantos, Vadillo-Pérez, & Jiménez-Gavilán, 2013; Apitz, Degetto, & Cantaluppi, 2009; Masetti, Sterlacchini, Ballabio, Sorichetta, & Poli, 2009; Peh, Miko, & Hasan, 2010). For the assessment of background concentration, there are numerous different statistical methodologies recently implemented. The clean stream approach, erosion model, sediment approach, monitoring data approach, and their modifications are some of the widely used approaches for the determination of background concentration. In the clean stream approach, background concentration is assumed as the concentration determined in a pristine environment rather than the calculated value (Oste, Zwolsman, & Klein, 2012). According to the background assessment studies performed by Oste et al. (2012), in order to obtain reliable results from the clean stream approach, it should be ensured that whether the target river is truly pristine or not. However, it is considerably complex to define a river environment as pristine due to the constant and complex interaction mechanism of the river bodies with the surrounding environment. Therefore, the accuracy of the clean stream approach is questionable. In the sediment method, background concentrations are determined by using sediment partition coefficients (Kps) in order to predict the amount of release from sediments to freshwater sources (Vijver, Spijker, Vink, & Posthuma, 2008; Oste, Zwolsman, & Klein, 2012). This method can be reasonable when well-established Kp values and the data from undisturbed sediment are available. However, since the reliability of the method strictly depends on the value of Kp, this method is quite simple to implement, which creates uncertainty in the results.

As explained in the previous sections, low-level anthropogenic fractions are unlikely to be completely removed from the monitoring data. However, a statistical approach to be followed for the determination of NBCs should aim the elimination of major anthropogenic pressures and mitigation of diffuse anthropogenic inputs from the data as much as possible. For the implementation of this purpose, a low percentile analysis of the monitoring data was conducted in order to determine NBCs of the selected metals and metalloids. The percentile analysis can be conducted on a low-level basis (5^{th}, 10^{th} percentile) or high-level basis (50^{th}, 90^{th} percentile) depending on the quantity and quality of available data as well as the level of disruption by anthropogenic pressures. Peters et al. (2012) stated that high percentile analysis, like usage of 50^{th} and 90^{th} percentile, leads to misleading data interpretation since high percentile analysis is more suitable for the data obtained from the environment that is not subjected to any anthropogenic sources, including minor diffuse anthropogenic inputs. In other words, the study environment should be entirely pristine for the usage of high percentile analysis. In this respect, in this study, the low percentile analysis (5^{th} percentile) of monitoring data was performed in order to stick to a conservative approach for the determination of river basin specific NBCs of metals and metalloids. The implementation of low percentile analysis was carried out with the integration of different statistical tests and approaches. Within the context of this study, descriptive data analysis and outlier detection tests were also employed. Furthermore, the data treatment strategy was developed for the observations below LOD values with the establishment of three different approaches. Besides these practices, the river basin specific EQS derivation methodology, which is described in detail in Section 2.3.4, was also addressed within the scope of this study.

2.3 Methodology

Within the scope of the project entitled "Management of Point and Diffuse Pollution Sources in the Yeşilırmak River Basin" with project code of 115Y013, a comprehensive water quality monitoring study was carried out in the Yeşilırmak River Basin, which includes sampling every three months over a two year period. The analysis of the water samples collected by a team from Munzur University was carried out by the Institute of the Scientific and Technological Research Council of Turkey (TUBITAK) Marmara Research Center. In the present thesis study, using the water quality data from the Project mentioned above, a basin-specific NBCs assessment task was performed for 26 metals and metalloids, which were presented within the water quality data from the Yeşilırmak River Basin. The stepwise procedure was followed within the context of this study. First, datasets for each metal and metalloid were prepared for the further analysis steps by selecting definite sampling points based on location in order to obtain datasets that are suitable for statistical analysis. In addition, non-detect percentages of each metal and metalloids were calculated as a part of the data preparation step. Then, an outlier test was employed for the exclusion of anomalies that exist in the datasets. Subsequently, a low percentile analysis of monitoring data was conducted together with the establishment and implementation of three different approaches in order to handle non-detect observations. As a result of low percentile analysis with different approaches, basin-specific NBCs were calculated. Finally, basin-specific EQS values were derived on the basis of implementation criteria imposed by the Regulation on Surface Water Quality (Official Gazette No:29797, 2016). The detailed implementation procedures of these steps will be explained in the following sections.

2.3.1 Data Selection and Compilation

When determining NBCs, the water quality data from locations that are least affected by anthropogenic sources should be included in the datasets in order to prevent the misinterpretation of statistical data. Thus, in using the water quality data obtained from the monitoring study carried out in the Yeşilırmak River Basin, care was taken not to include the sampling points under the influence of massive inputs released from anthropogenic sources. The primary purpose of the data preparation step is to exclude the data which are affected by these anthropogenic sources as much as possible. Therefore, the water quality data collected from the exit of the industrial and municipal wastewater treatment plants were eliminated from the datasets. This elimination contributes to reducing uncertainty in the background concentration estimation because the main focus of this study is to observe the natural impact of the metals on the river basin. After screening the data thought to be under the influence of anthropogenic sources, approximately 390 data points remained for the statistical analysis of the metal and metalloids data. Peter et al. (2012) stated that background concentration derivation requires at least 50 data points in order to reach accuracy to a certain extent. In this study, despite the data elimination, the adequate number of data condition was met for the reliable statistical analysis. The adequate number of data is a quite critical issue for the applicability of data analysis. The low percentile covers a small portion of data; thus, the number of data should be as high as possible for reliable data analysis. In this study, a high number of data was attained by incorporating the data obtained from the eight different measurement periods and from the various locations of the basin. In this way, the impact of concentration changes due to seasonal variations was also included in the datasets.

Another issue related to data reliability is the measurement results, which are lower than the LOD values (below-LODs/non-detects). These non-detect values present in the datasets should be treated in order to prevent uncertainty originated from the absence of these observations. In data analysis, sources of pollution are interpreted by implementing quantitative knowledge, which is hidden in measured concentration values. This knowledge is censored by non-detect values that exist in datasets. Non-detect data contribute to datasets in number while they lead to a bunch of missing knowledge by maintaining their presence in datasets. With regard to the degree of contribution to the dataset, the number of non-detect values is substantially vital since the extent of their presence can result in overestimation or underestimation of derived background values depending on the approach to how they are treated. Therefore, the percentage of the below-LOD values in the dataset of each metal was calculated to figure out the level of uncertainty present in each dataset. In this way, information on the non-detect value percentage enabled us to evaluate whether datasets are suitable for the percentile analysis or not. According to studies conducted by Peters et al. (2012), if non-detect values cover above 30% of an entire dataset, then the accuracy of percentile analysis will be poor, and also, the certainty of analysis will decrease at a certain level. Hence, these below-LOD values should be treated and included in datasets by practicing different methodologies depending on the percentage of below-LOD values. The treatment of below-LOD observations with the establishment of different approaches will be explained in the following sections.

2.3.2 Outlier Detection Test: Adjusted Tukey's Method

Another concern that affects the quality of datasets is the extreme values which are called "outliers". The outlier is a value that is extremely different from the rest of the data distribution (Ohio-EPA, 2012). Outliers may originate from several reasons like the existence of point anthropogenic inputs and/or measurement errors in the water quality data used (Rousseeuw & Hubert, 2011). Outlier removal not only provides the removal of misleading values from data but also enables us to clean data from the impacts of anthropogenic effects. However, US EPA (2009) pointed out that discarded outliers may be a part of the background population, and there is a probability that these outliers may be generated from natural sources even if they are highly erratic compared to the rest of the data distribution. Therefore, the selected outlier detection method should not be restrictive in order to prevent the loss of real natural-based observations that belong to the dataset and meaningful part of the background concentration. Outliers disrupt data distribution, and they generally cause overestimation or underestimation of statistical analysis. In this study, the detection of outliers was performed based on a methodology that eliminates values that are apparently high in magnitude without being strict because only having a high concentration is not enough for the indication of anthropogenic inputs.

For the selection of the outlier detection method to be implemented, qualitative and quantitative characteristics of data should be taken into account based on some criteria like the number of data and type of data distribution. The Standard Deviation Method, Dixon's Method, and Rosner Method are some of the techniques that are developed for outlier detection. Most of these methods require a low number of data and homogeneously distributed datasets. However, with regard to the data obtained from the Yeşilırmak River Basin, it was examined that these methods cannot be implemented due to the high number of data and non-homogeneous data distribution of the available datasets, which do not satisfy the requirements of these techniques. Besides, the range between the individual value of the data is quite wide; hence, this situation also leads to sharp fluctuations through the dataset. In other words, the difference between the smallest and largest value of the available data is considerably high for the case of measurement results from the Yeşilırmak River Basin. This situation creates the need for an advance and relatively strict method that does not cover a broad range of data as an outlier. On the basis of this idea, the adjusted Tukey's Method, which is preferred for high in number, widely ranged, and non-homogeneously distributed datasets was implemented for outlier detection purposes.

The conventional methods mentioned above assume a large portion of the dataset as an outlier and exclude these values from the dataset. On the other hand, the Adjusted Tukey Method provides a substantially strict approach by eliminating only excessively high-magnitude data points. In this study, upper and lower limits were determined for the detection of outlier values present in the datasets of each metal and metalloid by implementing the Adjusted Tukey's Method. Since the below-LOD values were treated with the three different approaches as explained in the previous section, the lower limits of the data were not further treated within the context of the outlier detection method. Therefore, only upper limits were evaluated as the main concern for outlier detection. One of the main advantages of this method is to provide a reliable high upper limit for the exclusion of outliers so that any risk to loose data which may belong to natural input was prevented by considering largely ranged characteristic of the existing data. By using Equation (1), data values that exceed the upper limit determined by the Adjusted Tukey's Method were excluded from the datasets (European Commission Joint Research Center, 2015).

$$\text{Upper Fence Limit} = (\text{3rd Quartile}) + \text{k} * (\text{Interquartile}) \qquad (1)$$

where,

1st Quartile (Q1)= 25% of the numbers in the dataset

3rd Quartile (Q3)= 75% of the numbers in the dataset

Interquartile (IQR) = Q3-Q1

K=1000 (constant for non-normal distribution)

In principle, the upper fence limit is given in Equation (1) defines the maximum distance from the median value of the dataset. As it is illustrated in Figure 2.1, the distance between the upper fence limit and the lower fence limit represents the maximum allowable data spread. Values above this boundary are defined as outliers. This approach gives information about the extent of deviation from the common data distribution. Another compound of Equation (1) is the K constant, which determines the extent of interquartile spread. This constant can be used as a different numerical value in different versions of the Tukey's Method from 10 to 1000, depending on the characteristics of data. However, small K values bring about a quite narrow spread up to the upper fence limit that results in the exclusion of a large part of the dataset.

Therefore, the adjusted version of the Tukey's Method, which provides rigorous and high certainty practice, was preferred to apply for outlier determination by suggesting the use of high-magnitude constant (K=1000). The European Commission Joint Research Center (2015) reported that the use of K=1000 enables datasets to protect variation knowledge that is part of the data population by ensuring that a maximum of 31 % of data population is discarded as an outlier. Moreover, the impact of elevated data on the dataset was decreased further by using low percentile analysis for the determination of background concentration. Hence, the compensative approach was followed by implementing the only removal of extremely elevated outliers before conservative low percentile analysis. Within the scope of this principle, in the outlier test, it was aimed to obtain high distance upper limit, which is desirable for widespread datasets in order to implement sound practice while eliminating outliers.

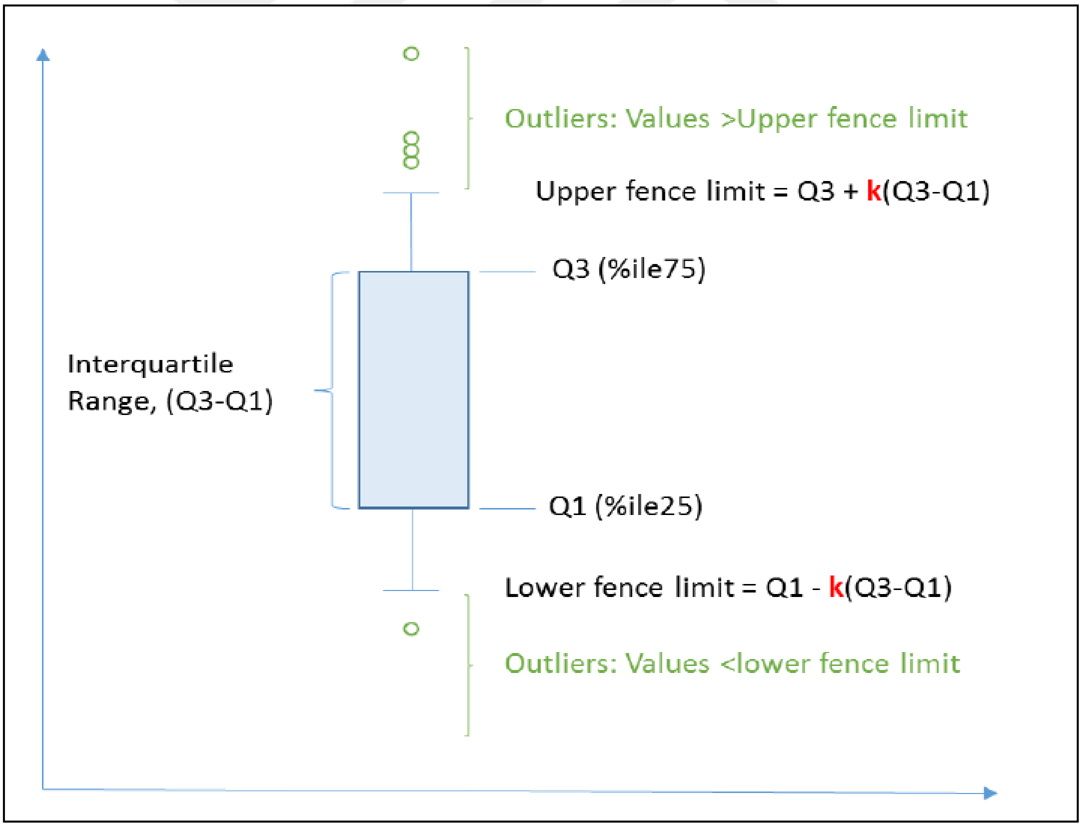

Figure 2.1. Visual Representation of Outlier Detection Methodology by Adjusted Tukey's Method (European Commission Joint Research Center, 2015)

2.3.3 Below-LOD Treatment and NBC Determination

As it was mentioned in the previous sections, the explicit differentiation between the effects of diffuse anthropogenic inputs and natural inputs on the data is notably hard to detect. However, low percentile usage enables to reduce the reflections of anthropogenic sources on the calculated NBCs. In other words, a low percentile analysis of monitoring data can achieve to make a conservative assessment of NBCs by minimizing the effects of minor anthropogenic inputs on the data. On the other hand, usage of high percentile comprises highly elevated values in the dataset as the background value. If the study area is entirely free from anthropogenic effects, which is a rare case, high percentile usage may be applicable since, in this case, the inclusion of highly elevated values will also represent data from a purely natural environment. In this study, high percentile analysis, like usage of 50th and 90th percentile, is not preferred to implement on the data since the Yeşilırmak River Basin is not entirely pristine environment despite the elimination of the sampling results that represent major point sources. For the calculation of NBCs, the 5th percentile analysis was employed by establishing and comparing different below-LOD handling approaches.

In order to evaluate the effects of non-detect existence within the datasets on percentile analysis, non-detect values were treated by implementing different approaches. Based on this purpose, the observations below-LOD were incorporated into the datasets by following three different approaches listed below.

- *Approach 1*: Removal of below-LOD data points
- *Approach 2:* Replacement of non-detected value with reported LOD value
- *Approach 3:* Replacement of non-detected value with half of LOD value

Depending on the percentage of below-LOD values, these three approaches may generate similar or different percentile values. The implementation of all these three approaches has a probability of creating a bias in the dataset. However, there will always be a bias in any of the cases. Thus, the main aim is to reach a less biased approach by comparing the results of these approaches.

2.3.4 Derivation of Basin Specific EQSs

After the calculation of NBCs by comparing the three approaches, the EQSs specific to the Yeşilırmak River Basin were derived based on Equation (2) and Equation (3) within the context of the Regulation on Surface Water Quality (Official Gazette No:29797, 2016).

If NBC is below the existing EQS value, then the environmental target (ET) is equal to existing EQSs;

$$\mathrm{NBC} < \mathrm{EQS} \longrightarrow \mathrm{ET} = \mathrm{EQS} \tag{2}$$

If NBC is equal or above existing EQS, then ET is the sum of the NBC and existing EQS;

$$\mathrm{NBC} \geq \mathrm{EQS} \longrightarrow \mathrm{ET} = \mathrm{NBC} + \mathrm{EQS} \tag{3}$$

where,

ET=Environmental Target (Basin-Specific Environmental Quality Standard)

NBC=Normal Background Concentration

EQS=Existing Environmental Quality Standard

"Environmental Target" term used in the above equations are specified by the Regulation on Surface Water Quality. This "Environmental Target" term implies indeed "River Basin Specific EQS," which is derived on the basis of currently existing EQS values. Currently-existing EQS values, which are not basin-specific, are presented by the Regulation on Surface Water Quality under the guide of the EU WFD (2000/60/EC) and EQS Directive (2008/105/EC). In light of these legislations, basin-specific NBCs and basin-specific EQSs were derived in this study.

2.4 Results and Discussion

2.4.1 Results of Data Compilation and Characterization

For each of the 26 metals and metalloids present in the Yeşilırmak River Basin, the data percentages below-LOD were calculated in order to figure out how much of the datasets were occupied by these values. The results are provided in Table 2.1. As can be seen in Table 2.1, the below-LOD percentage is 38% for the dataset of Se and above 50% for the datasets of Cd, Be, Ti, S^{-2}, CN^{-}, Hg, and Sn, which are demonstrated in the colored part of the table. This situation results in uncertainty in the datasets; thus, these datasets with a high percentage of non-detects were treated by employing the three different approaches (removal of below-LOD, replacing below-LOD with reported LOD, and replacing LOD with LOD/2). The datasets of the rest of the metals and metalloids (B, Fe, Si, Mg, Al, As, Ba, Co, Cr, Cu, Ni, V, Zn, Mn, Pb, Ca, Sb, Ag) consist of quite a few non-detects which changes between 0% to 5.1%. Implementation of the approaches determined for the handling of the non-detects is not required for these metals and metalloids since a very small portion of their datasets are under the LOD values. In other words, for the datasets of metals and metalloids with low non-detects, the results of percentile analysis will not be affected by the usage of below-LOD dealing approaches. These low non-detect percentages provide relatively reliable data interpretation. Regarding high below-LOD percentages, the almost entire dataset of Hg and Sn consist of non-detect values which are responsible for 96.2% (10 observation detected out of 266), and 98.5% (six observation detected out of 390) of the datasets of each metal, respectively. In this case, the percentile analysis results of these metals will be notably affected by the usage of different below-LOD handling approaches, which will be discussed in the following sections.

Table 2.1 Below-LOD Percentages of Datasets for Metals and Metalloids

Metals and Metalloids	**Total Number of Data**	**Number of Data Below-LOD**	**Percentage of Data Below-LOD, %**
B	390	0	0.0
Fe	390	0	0.0
Si	390	0	0.0
Mg	384	0	0.0
Al	390	2	0.5
As	390	2	0.5
Ba	390	2	0.5
Co	390	2	0.5
Cr	390	2	0.5
Cu	390	2	0.5
Ni	390	2	0.5
V	390	2	0.5
Zn	390	2	0.5
Mn	308	2	0.6
Pb	390	3	0.8
Ca	384	11	2.9
Sb	390	14	3.6
Ag	390	20	5.1
Se	308	117	38.0
Cd	390	261	66.9
Be	390	270	69.2
Ti	384	312	81.3
S^{-2}	308	274	89.0
CN^{-}	348	315	90.5
Hg	266	256	96.2
Sn	390	384	98.5

2.4.2 Outlier Detection by Adjusted Tukey's Method

For 26 metals and metalloids, the outlier test was performed in order to detect and remove extremely elevated observations if they exist within the datasets. Based on this target, the Adjusted Tukey's Method was selected by taking into consideration data adequacy and compatibility with background determination technique (low percentile analysis) to be performed. The most significant characteristic of this method is to provide the detection of only abnormally high concentration values within the datasets. By implementing this restrictive method, it was aimed to avoid massive data exclusion from the datasets since the concentration variations in the datasets will also be further decreased during the low percentile analysis, which is discussed in Section 2.4.3. In this way, the impacts of the outlier test and low percentile analysis on the datasets were compensated to a certain extent. The calculated statistical elements of the Adjusted Tukey's Method are presented in Table 2.2. The red-colored row given in Table 2.2 represents having data points higher than the calculated upper fence limit.

Table 2.2 Calculation Results of Major Statistical Elements of the Adjusted Tukey's Method for Metals and Metalloids

Metals and Metalloids	**1st Quartile**	**3rd Quartile**	**Interquartile**	**Upper Fence Limit**
Zn (µg/L)	7.82	42.51	34.69	34733
Ag (µg/L)	0.05	0.19	0.14	137
Al (µg/L)	101.40	528.35	426.95	427474
As (µg/L)	1.96	6.15	4.19	4194
B (µg/L)	131.03	267.86	136.83	137102
Ba (µg/L)	47.06	79.04	31.98	32060
Be (µg/L)	0.02	0.04	0.02	19
Cd (µg/L)	0.03	0.08	0.05	54
Co (µg/L)	0.21	1.09	0.88	877
Cr (µg/L)	0.98	3.93	2.95	2953
Cu (µg/L)	14.83	20.32	5.49	5509

Table 2.2 (cont'd)

Metals and Metalloids	1^{st} Quartile	3^{rd} Quartile	Interquartile	Upper Fence Limit
Fe (µg/L)	174.41	866.56	692.15	693012
Mn (µg/L)	17.44	101.58	84.14	84245
Ni (µg/L)	2.25	6.96	4.71	4720
Pb (µg/L)	1.10	3.68	2.58	2584
Sb (µg/L)	0.46	2.99	2.53	2537
Se (µg/L)	0.16	1.11	0.94	944
Sn (µg/L)	5.00	5.00	0.00	5
V (µg/L)	2.47	5.73	3.26	3269
Hg (µg/L)	0.07	0.07	0.00	-
Si (µg/L)	4622.50	7600.00	2977.50	2985100
Ti (µg/L)	3.84	3.84	0.00	-
Ca (mg/L)	51.16	43616.34	43565.18	43608801
Mg (mg/L)	19.54	8776.17	8756.64	8765412
CN^- (µg/L)	0.5	0.5	0	-
S^{-2} (µg/L)	0.5	0.5	0	-

When Table 2.2 is examined, extremely high values of upper fence limits can be seen clearly. The main reason behind these high levels of upper fence limits is K=1000 constant, which enables to discard only anomalies of the datasets rather than excluding the extended portion of the data. As a result of the main logic of this practice, it was calculated that the upper fence limit is exceeded only by the data of Zn out of all metals and metalloids. Except for Zn, the calculated upper fence limits (Table 2.2) are not exceeded by the data points of rest of the metals and metalloids. It was detected that the datasets of remaining metals and metalloids do not include extremely abnormal values. However, it does not mean that datasets of these metals and metalloids do not have any elevated concentration values since these elevated concentrations are not extremely abnormal to exceed upper limits despite their existence in the datasets. These elevated values still exist in the datasets, but their influence on the datasets will be eliminated by the low percentile analysis step. When compared to other metals and metalloids present in Table 2.2, it can be seen that Ca and Mg have noticeable high upper fence limits. The reason for this difference is that Ca and Mg are major elements that exist in nature, typically with high concentration values, which are represented as mg/L. However, the rest of the metals and metalloids present in nature as minor and trace elements with µg/L ranges. Consequently, this huge gap between upper fence limits can be explained by the difference between abundance levels of metals and metalloids in nature.

As it is demonstrated in Figure 2.2, the upper fence limit for the outlier detection of Zn dataset was calculated as 34733 µg/L, which is extensively exceeded by the outlier value of 100519 µg/L. In the dataset of Zn, the first largest data value before this outlier is 737 µg/L, which is remarkably low compared to the outlier value. This huge gap also shows how anomalous the detected outlier data compared to the entire dataset of Zn. As a result of this outlier test, the detected outlier value was discarded from the dataset of Zn in order to prevent sharp deviations from the accuracy of low percentile analysis results.

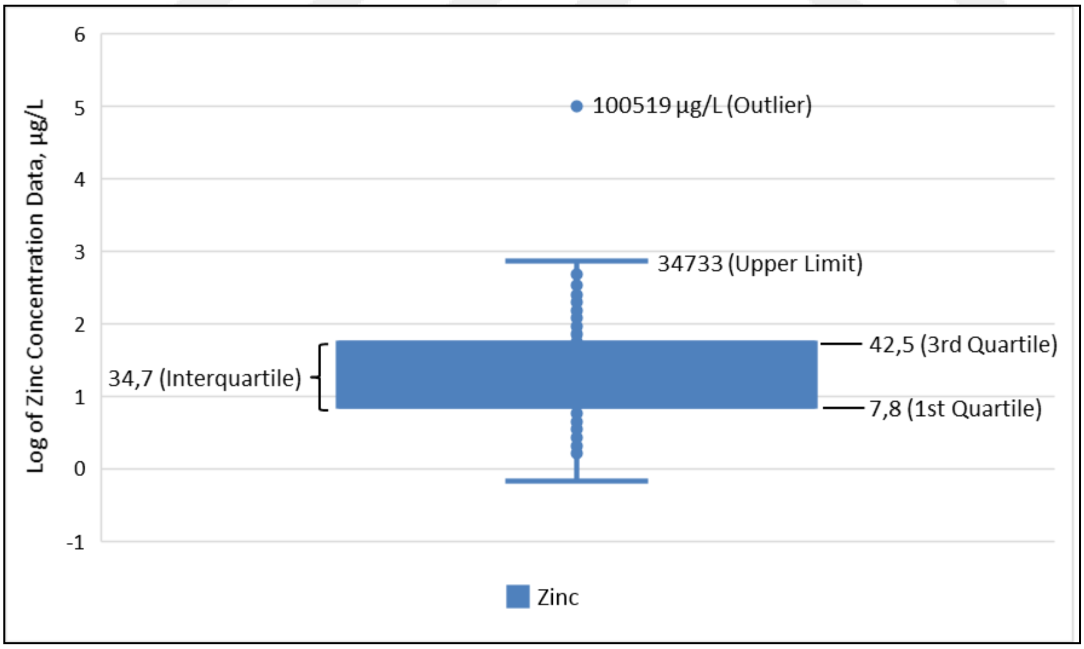

Figure 2.2 Outlier Detection Plot for the Dataset of Zn

2.4.3 Calculation of Basin Specific NBCs by Implementation of Low Percentile Analysis with Three Different Approaches

The low percentile analysis was implemented in order to achieve conservative practice, which is one of the most critical requirements for the accurate determination of NBCs. Since the study environment is not solely pristine, existing anthropogenic effects should be strictly eliminated from the datasets. This strict elimination can be accomplished with a conservative characteristic provided by the 5^{th} percentile analysis. The 5^{th} percentile analysis was conducted with the implementation of different approaches. As it was mentioned in the previous sections, below-LOD observations in the datasets should be handled in order to prevent uncertainty caused by the missing data points. For this purpose, three different approaches (Approach 1: removal of below-LODs, Approach 2: replacement with reported LOD, Approach 3: replacement with half of LOD) were employed during the application of the 5^{th} percentile analysis. The results of the low percentile analysis with the use of these approaches are given in Table 2.3.

Table 2.3 Results of Low Percentile Analysis for Three Different Approaches

Metals and Metalloids	5th Percentile Results for Approach 1, µg/L	5th Percentile Results for Approach 2, µg/L	5th Percentile Results for Approach 3, µg/L	Below-LOD% Range
B	55.94	55.94	55.94	0
Fe	62.58	62.58	62.58	
Si	1316.00	1316.00	1316.00	
Mg	6.87	6.87	6.87	
Al	46.51	45.59	45.59	<5%
As	1.03	1.02	1.02	
Ba	31.92	31.10	31.10	
Co	0.09	0.09	0.09	
Cr	0.53	0.51	0.51	
Cu	11.78	11.64	11.64	
Ni	1.02	0.96	0.96	
V	1.54	1.50	1.50	
Zn	3.84	3.71	3.71	
Mn	4.98	4.87	4.87	
Pb	0.74	0.72	0.72	
Ca	37.00	33.39	33.39	
Sb	0.20	0.14	0.14	
Ag	0.03	0.02	0.01	
Se	0.40	0.33	0.16	>35%
Cd	0.06	0.06	0.03	
Be	0.04	0.04	0.02	
Ti	8.26	7.67	3.84	
S^{-2}	2.00	1.00	0.50	
CN^{-}	1.09	1.00	0.50	
Hg	*	0.13	0.07	
Sn	*	10.00	5.00	

*Inadequate Data Number

As it is presented in Table 2.3, the gap between the 5th percentile results of different approaches increases with an increase in below-LOD%, as expected. Colored metals and metalloids in the table represent datasets having below-LOD observations greater than 35%. The effect of the approaches on the 5th percentile results can be seen more specifically for colored metals and metalloids since datasets of these metals and metalloids have higher below-LOD percentages. The comparison of these three approaches is demonstrated in Figure 2.3 (for metals and metalloids having below-LODs>35%) and Figure 2.4 (for metals and metalloids having below-LODs<5%). In general, 5th percentile results reach their highest value when Approach 1 is implemented because the removal of below-LOD observations leads to the decrease in the number of data nearly for all metals and metalloids given in Table 2.3. However, the degree of 5th percentile increase is remarkably higher for the metals having below-LODs>35% compared to the ones having below-LODs<5%. According to a study conducted by Peter et al. (2012), the removal of below-LOD observations brings about an upward bias of low percentile results. In our case, upward bias was also observed when Approach 1 is applied by excluding below-LODs.

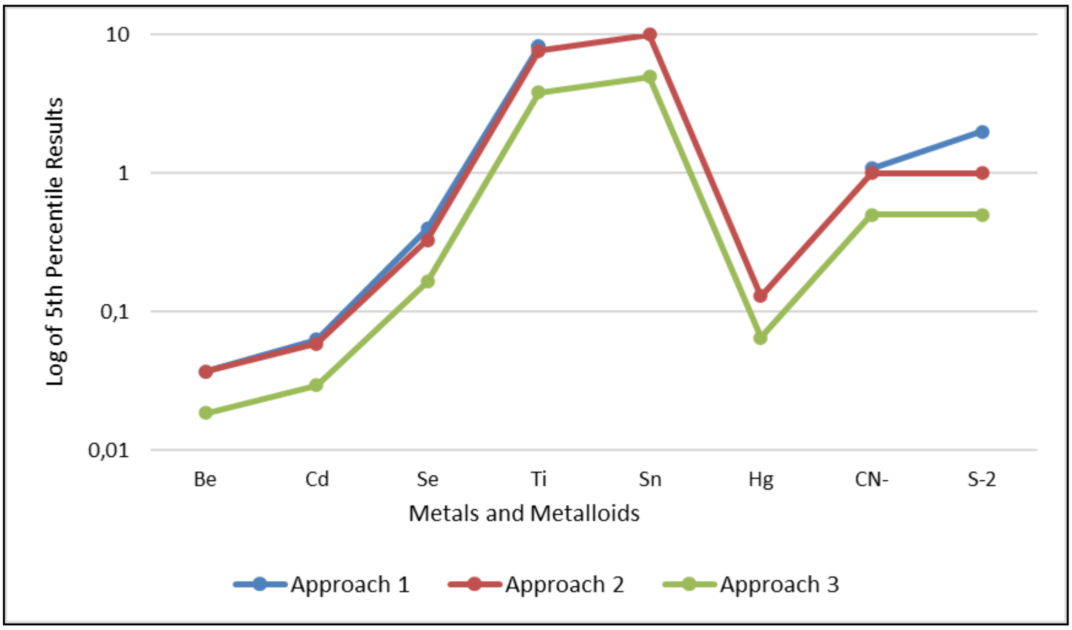

Figure 2.3 Comparison of Approaches for Metals and Metalloids Having below-LOD > 35%

Figure 2.3 presents the comparison of three approaches for the metals and metalloids having LOD>35%. As can be seen, Approach 1 does not apply for Sn and Hg because the amount of data of these metals becomes inadequate to perform low percentile analysis when below-LODs are eliminated from their datasets. After the implementation of Approach 1, the number of data points decreased from 266 to10 for Hg and from 390 to six for Sn. These numbers of data values are substantially low to perform percentile analysis. Therefore, it seems that there are two suitable options (Approach 2 and Approach 3) for the background calculation of Hg and Sn. When the results of Approach 2 are examined, it can be seen that Approach 2 generates considerably higher concentrations than Approach 3 and slightly lower concentrations than Approach 1. However, this difference is valid for metals having below-LOD>35% (Figure 2.3). For the metals below-LOD<5%, there is no significant difference between the results of different approaches since the non-detect values are responsible for a very small portion of their datasets.

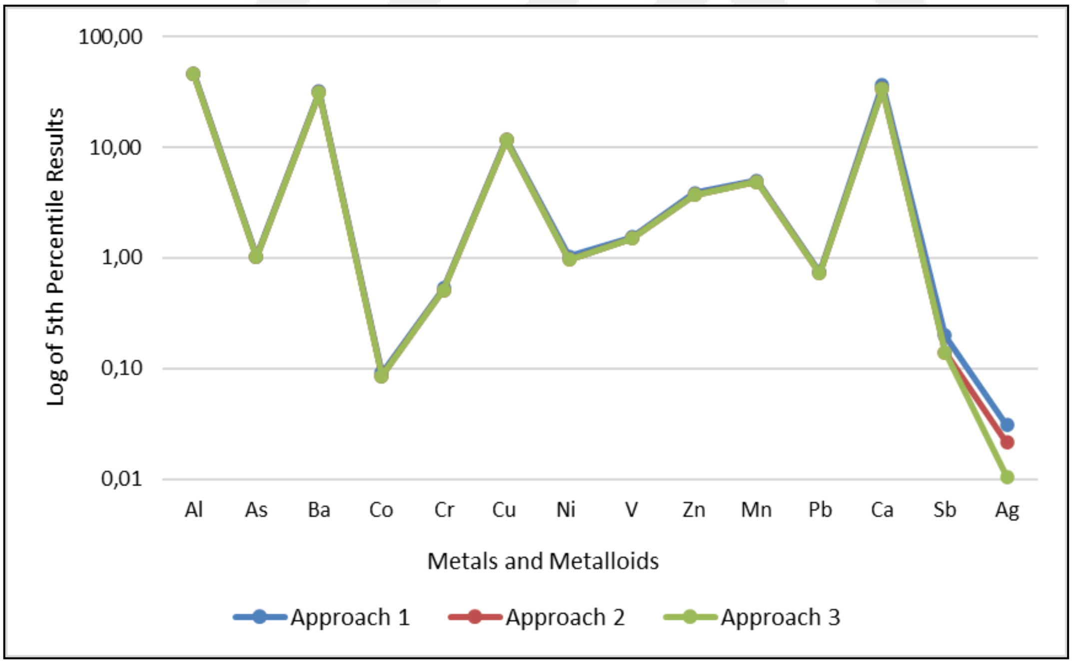

Figure 2.4 Comparison of Approaches for Metals and Metalloids Having below-LOD < 5%

As it is shown in Figure 2.4, percentile results obtained from the metals having below-LODs<5% are not remarkably different from each other in all three approaches since below-LOD percentages are too low to have a contribution on datasets. In other words, removal or replacement of these non-detects does not affect the results of the percentile analysis of these metals (below-LODs<5%) due to the very low existence of non-detects in number. Indeed, these low amounts of non-detects are an indicator of higher quality data compared to datasets with a high amount of non-detects. In Figure 2.4, the difference between the approaches can only be seen for Sb and Ag, which have relatively higher non-detects compared to other metals grouped in below-LODs<5%. In this case, results of Sb and Ag are ordered as Approach 1>Approach 2>Approach 3, which is also the same increase order for the metals in Figure 2.3.

As it is seen from the case of Approach 1 in Figure 2.3, the exclusion of below-LOD values causes a sudden increase in percentile results of metals having below-LOD>35%, which leads to an overestimation since a considerable portion of the data is ignored in this approach. For the case of Approach 2, percentile results of metals having below-LOD>35% are slightly lower than Approach 1, but still high and create upward bias. When compared to Approach 1 and Approach 2, Approach 3 produced relatively lower and reasonable outcomes as a result of replacing non-detects with small numerical values, which provides precautionary practice. This approach may bring about downward bias due to its lowering effect on percentile results, but the determination of NBCs requires conservative and strict procedures in order to eliminate major anthropogenic impacts and also to mitigate diffuse and historical anthropogenic impacts on the datasets. After the comparison of the approaches, it was concluded that this conservative concept is obviously provided by Approach 3. Therefore, Approach 3 was determined as the most applicable practice for the purpose of dealing with below-LOD data. As a result of these procedures, the NBCs were determined as 5^{th} percentile results of Approach 3, which is given in Table 2.3.

At the end of the discussion, one last issue related to the results of the approaches is needed to be clarified. This issue is the uncertainty created by the datasets which have high below-LOD percentages since these datasets are prone to generate percentile results that are equal or near to recorded LOD values. However, when general data distribution in the datasets of these metals is examined, it can be seen that, except below-LOD values, the rest of the data observations are also significantly low. Therefore, when distribution characteristics of the datasets are taken into account, it is acceptable that Approach 2 and Approach 3 create results near to recorded LOD values. When removal of below-LODs is applied, strong upward bias was observed due to a lack of a massive portion of data lead to misleading results. Approach 2 also generates an upward bias. Therefore, in spite of uncertainties for some of the metals, Approach 3 seems as the best option. The USEPA (2017) also recommends the replacement of below-LOD observations with LOD/2 in order to increase the reliability of the datasets.

2.4.4 Derivation of Basin Specific EQSs

For the derivation of river basin specific EQS values, Equation (2) and Equation (3) were implemented with the assessment of the calculated NBC results and the existing EQS values for each of the metals and metalloids. In Table 2.4, the calculated NBCs and the existing AA-EQS values of metals are compared in order to detect the exceedance level of the existing AA-EQS values. Except for Al, Cu, and Fe, for the rest of the metals and metalloids given in Table 2.4, it can be seen that calculated NBC values are lower than the existing AA-EQS values. Regarding the established methodology in Equation (2), river basin specific EQS values were determined as equal to the existing EQS values for Ag, As, B, Ba, Be, Cd, Co, Cr, Ni, Pb, Sb, Sn, V, Zn, Hg, Si, Ti, and CN^-.

$$\mathrm{NBC} < \mathrm{EQS} \longrightarrow \mathrm{ET} = \mathrm{EQS} \tag{2}$$

As it is provided in Table 2.4, it was calculated that the highest NBC value in the Yeşilırmak River Basin belongs to Si as 1316 µg/L, which is followed by Fe, B, and

Al as 63 µg/L, 56 µg/L, and 46 µg/L, respectively. Even though Si and B are among the metals that have the highest NBC values in the river basin, the NBC values of these metals are below their existing EQS values (Table 2.4); therefore, their basin-specific EQS values were determined as equal to their existing EQS values. The red-colored rows given in Table 2.4 represent the metals that have NBC values higher than their existing EQS values.

Table 2.4 Comparison of AA-EQS and 5th Percentile Results

Metals and Metalloids	Number of Data	Maximum Value (µg/L)	Minimum Value (µg/L)	NBC (µg/L)	AA-EQS (µg/L)
Al	390	61485.7	0.256	45.591	2.2
Cu	390	677.3	0.132	11.643	1.6
Fe	390	93282.6	4.117	62.600	36
Ag	390	2.5	0.011	0.011	1.5
As	390	520.1	0.105	1.016	53
B	390	2597.7	10.229	55.900	707
Ba	390	887.1	0.224	31.096	680
Be	390	3.1	0.019	0.019	2.5
Cd	390	45.6	0.030	0.030	0.08
Co	390	65.5	0.013	0.086	0.3
Cr	390	135.6	0.100	0.515	1.6
Ni	390	210.9	0.037	0.963	4
Pb	390	115.4	0.033	0.724	1.2
Sb	389	196.1	0.060	0.140	7.8
Sn	390	47.0	5.0	5.0	13.0
V	390	206.1	0.011	1.501	1.6
Zn	389	737.1	0.334	3.706	5.9

Table 2.4 (cont'd)

Metals and Metalloids	Number of Data	Maximum Value (µg/L)	Minimum Value (µg/L)	NBC (µg/L)	AA-EQS (µg/L)
Hg*	266	0.400	0.065	0.065	0.070*
Si	384	55650.0	121	1316	1830
Ti	384	886.9	3.835	3.835	26
CN^-	348	1739.0	0.500	0.500	1.2
Mn	308	2653.0	0.050	4.873	-
Se	308	124.3	0.165	0.165	-
S^{-2}	308	9.0	0.500	0.500	-
Ca**	384	327779.6	15.000	33.388	-
Mg**	384	86529.5	0.462	6.900	-

*For Hg, maximum EQS value was used since there is no established AA-EQS for Hg.
**Since Ca and Mg are major elements existing in nature, these metals are presented in an unit of mg/L rather than µg/L.

As it can be seen in Table 2.4, it was determined that Al, Cu, and Fe have NBC values as 45.6 µg/L, 11.6 µg/L, and 62.6 µg/L that are greater than their AA-EQS values, which are 2.2 µg/L, 1.6 µg/L, and 36 µg/L, respectively. For these three metals, the basin-specific EQSs were calculated by summing the NBC values and the AA-EQS values according to Equation (3) provided in the previous sections.

$$\mathrm{NBC} \geq \mathrm{EQS} \longrightarrow \mathrm{ET} = \mathrm{NBC} + \mathrm{EQS} \tag{3}$$

Within the scope of this methodology, as it is presented in Table 2.5, the basin-specific EQS values of the Yeşilırmak River were derived as 47.8 µg/L, 13.2 µg/L and 98.6 µg/L for Al, Cu, and Fe, respectively. For the rest of the metals and metalloids, the basin-specific EQS values determined as equal to the existing EQS values (pre-defined general EQSs).

Table 2.5 Results of Basin Specific EQS Values for the Yeşilırmak River

Metals	NBC, µg/L	Pre-defined General EQS, µg/L	Basin Specific EQS, µg/L
Al	45.6	2.2	47.8
Cu	11.6	1.6	13.2
Fe	62.6	36.0	98.6
Ag	0.011	1.500	1.500
As	1.016	53.000	53.000
B	55.9	707.0	707.0
Ba	31	680	680
Be	0.02	2.50	2.50
Cd	0.03	0.08	0.08
Co	0.09	0.30	0.30
Cr	0.52	1.60	1.60
Ni	0.96	4.00	4.00
Pb	0.72	1.20	1.20
Sb	0.14	7.80	7.80
Sn	5.0	13.0	13.0
V	1.5	1.6	1.6
Zn	3.7	5.9	5.9
Hg*	0.065	0.070*	0.070*
Si	1316	1830	1830
Ti	3.8	26.0	26.0
CN^-	0.5	1.2	1.2
Mn	4.87	-	-
Se	0.17	-	-
S^{-2}	0.50	-	-
Ca**	33.39	-	-
Mg**	6.90	-	-

*For Hg, maximum EQS value was used since there is no established AA-EQS for Hg.
**Since Ca and Mg are major elements existing in nature, these metals are presented in an unit of mg/L rather than µg/L.

2.5 Conclusion and Recommendations

Surface water contamination that originates from metals and metalloids emerged as a vital issue that needs to be handled in order to protect the natural environment and human health and also to enhance the current status of the water environment. Metals and metalloids are adversely affecting surface water quality due to the high concentrations present in the surface water bodies. However, these metals can also be an essential part of the natural environment that needs to maintain their existence at certain levels in different environmental compartments. When their role in the ecological cycle and their nutrient status for particular living organisms are taken into account, the absence of these metals may lead to the devastation of ecological balance. On the other hand, metal contribution to the natural environment is continuously increasing via anthropogenic sources. If necessary precautions for the reduction of these metals are not taken with a systematical management strategy, disruption of the natural environment becomes inevitable. As a result, both high and low concentration levels of metals may generate substantial risk for the freshwater environment. In other words, metals can be a threat but also be a crucial element for ecological balance depending on the management strategies developed in order to maintain sustainable levels of these metals in freshwater bodies.

Within the scope of this study, the Yeşilırmak River Basin is the target water body that requires basin-specific management implementations. One of the most substantial implementations is the establishment of river basin specific EQSs in order to improve and protect the quality of the receiving body. For the fulfillment of this implementation, the main requirement is the derivation of basin-specific NBCs. Within the context of this study, river basin specific EQSs and river basin specific NBCs were calculated for the Yeşilırmak River Basin. During this procedure, data compilation and analysis, outlier test, below-LOD treatment with the establishment of three different approaches, low percentile analysis for river basin specific NBC derivation, and also river basin specific EQS derivation were performed by following comprehensive data management practices. This study established a progressive basis for the development of efficient remediation techniques, reliable risk assessment strategies, the establishment of realistic and goal-oriented discharge limits, and receiving body standards specific to the Yeşilırmak River Basin.

The main conclusions drawn in this study are summarized below:

- Among the three approaches considered during the below-LOD treatment, the one where the replacement of below-LOD observations with LOD/2 (Approach 3) is implemented seemed as the best approach.
- Approach 1 (the removal of below-LOD observations) brought about an upward bias of low percentile results.
- Approach 2 (replacement of LOD with reported LOD value) also lead to overestimation of the low percentile analysis.
- The 5^{th} percentile results obtained for three approaches deviated more with datasets having higher below-LOD percentages.
- For the metals and metalloids having below-LOD percentage higher than 35%, Approach 2 generates considerably higher concentrations than Approach 3 and slightly lower concentrations than Approach 1.
- For the metals and metalloids having below-LOD percentage lower than 5%, there is no significant difference between the results of different approaches except Sb and Ag. For Sb and Ag, 5^{th} percentile results were calculated as in the order of Approach 1>Approach 2>Approach 3.
- When compared to Approach 1 and Approach 2, Approach 3 produced relatively lower and reasonable outcomes as a result of replacing non-detects with small numerical values, which provides precautionary practice.
- The results of 5^{th} percentile analysis show that the highest NBC value in the river basin belongs to Si as 1316 µg/L, which is followed by Fe, B, and Al as 63 µg/L, 56 µg/L, and 46 µg/L, respectively.
- For Ag, As, B, Ba, Be, Cd, Co, Cr, Ni, Pb, Sb, Sn, V, Zn, Hg, Si, Ti, and CN^- ,the calculated NBC values were determined as below their existing EQS values.

- For Ag, As, B, Ba, Be, Cd, Co, Cr, Ni, Pb, Sb, Sn, V, Zn, Hg, Si, Ti, and CN^- ,river basin specific EQS values were determined as equal to their existing EQS values.
- For Al, Cu, and Fe, NBC values were determined as above their existing EQS values.
- For Al, Cu, and Fe, river basin specific EQS values were derived as 47.8 μg/L, 13.2 μg/L, and 98.6 μg/L, respectively.

As a recommendation for future studies, uncertainties resulted from the quantity of available data for data analysis can be resolved by increasing the number of sampling studies over long measurement periods. Moreover, geological data, which reflects the natural characteristics of the basin, can be integrated into the study when available data is introduced for the Yeşilırmak River Basin. As a final suggestion, the complex interaction of metals through the air, groundwater, soil, and other different environmental compartments can be incorporated into the study by advanced modeling researches, which requires expert knowledge.

CHAPTER 3

AGRICULTURAL SOURCE IDENTIFICATION OF PESTICIDE POLLUTION IN YEŞİLIRMAK RIVER BASIN

3.1 Introduction

Global food production has been in progressive growth to meet the rapid increase in food demand, which is mainly supplied by agricultural activities. The dramatic increase in the need for agricultural production brings about various challenges related to the management of agricultural applications. The main concern arising from agricultural production is the devastation of the quality and quantity of agricultural products by the variety of insects, weeds, fungal diseases, mites, and the other different types of organisms responsible for disrupting the agricultural crops. For the reduction and elimination of these damages, pesticide spraying activities have been widely implemented in agricultural lands from past to present. Pesticides substantially serve as protection and yield enhancement mechanisms for agricultural crops. More specifically, when agrochemicals are sprayed on agricultural fields, they typically behave as a shield against the pest infestations, which occupy agricultural plants and seeds. In this respect, pesticides have become an indispensable part of today's agricultural management strategies. On the other hand, the detrimental effects of pesticides on the natural environment have gained critical importance in parallel with the drastically increasing pesticide consumption worldwide. One of the most significant issues associated with pesticide consumption is that insects, fungi, and other pest species can develop resistance to agrochemicals after a certain period of time. In other words, the pests observed in the agricultural fields start to be unaffected by the pesticide applications by the time of progress. Therefore, the amount of pesticides sprayed on the agricultural fields needs to be increased over time to overcome the resistance of the pests and ensure the functional protection of agricultural products. This situation constitutes a problem of a rapid increase in pesticide consumptions, which is followed by the severe accumulation of pesticides in the natural environment. Especially in freshwater environments, pesticide contamination has been adversely influencing both of the aquatic ecosystem and human health via the drinking water supply. Due to the intensive pesticide spraying activities, pesticides can reach the freshwater environment and maintain their existence for a long period of time. As a consequence, pesticide contamination in most of the river bodies has become a long-standing environmental concern that is required to be investigated and managed primarily at the source.

This thesis addresses the issue of pesticide pollution arising from agricultural activities in the Yeşilırmak River Basin by pursuing a comprehensive analysis and assessment approach. The amount and type of pesticides that occur in the freshwater environment considerably depend on the local farming practices performed in the surrounding environment of the polluted site. Thus, to take action concerning the excessive use of pesticides, the sources of pesticide pollution should be identified by following location-based assessments, which offer to accomplish the target-specific management strategies. Within the scope of this thesis, the spatial and temporal trends of the pesticide concentrations in the river were evaluated by analyzing the water quality data both across the entire basin and in the sub-divided small terrains that are characterized by their particular geographical, topographic, and climatic conditions in parallel with the localized agricultural profiles. In the case of the Yeşilırmak River Basin, these small terrains are represented by the districts that locate the water quality sampling stations in their boundaries. In this regard, within the context of this thesis, the source identification of the pesticide pollution was performed individually for each of the districts of the basin that embodies sampling stations within their boundaries. In order to fulfill an elaborative source identification regarding the pesticide pollution, this thesis has paid particular attention to the relation between the pesticide occurrence trends in the Yeşilırmak River Basin and the agricultural pesticide usage profiles of each district of the basin, which reflect the local agricultural characteristics and application trends of agrochemicals.

Throughout their pathway from the target site to the river, pesticides can interact with various environmental compartments, including air, soil, groundwater and also with the components of the biologic and chemical elements of nature. The complex interaction potential of pesticides with the surrounding environment is the major constraint to obtaining reliable source identification. In this regard, within the context of this study, the primary factors that have high potential to trigger the wash off the pesticides and influence both temporal and spatial occurrence trends of the pesticides were taken into account by detailed data analysis and evaluations. The major factors that were analyzed and assessed within the scope of this thesis are the soil and water half-lives of the pesticides (as a measure of persistence), the precipitation regimes of the districts and the entire basin, the soil adsorption capacities (as a measure of mobility) of the pesticides and the altitude of each district. As being one of the most effective driving force for pesticide runoff, the precipitation regime of each district was taken into account by analyzing and examining the relationship between the monthly average precipitation trend of each district and the months of the pesticide detections at the sampling stations of the corresponding districts. This thesis has also focused on the impact of the persistence and mobility of the pesticides on their spatial and temporal concentration trends. In this respect, the impact of soil sorption capacities of the pesticides on their spatial distribution and the impact of the soil and water half-lives of the pesticides on their temporal occurrence trend were analyzed across the basin. Furthermore, the relation between the altitudes of the districts and the diversity of the pesticide types that were observed at the sampling stations of the corresponding districts were analyzed and examined within the scope of this thesis.

3.2 Background

Due to the persistent, bioaccumulative, and toxic properties of the pesticides, the production and usage of most of the pesticides have been banned within the scope of the EU Regulation on Plant Protection Products (1107/2009/EC). In Turkey, the nationwide approval status of pesticide usage and production is governed by the Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides in Foodstuff (Official Gazette No: 29899, 2016). Despite their banned status, the vast majority of the pesticides have still been detected at high concentration levels in freshwater environments. So far, numerous studies have been performed regarding the evaluation and management of the point sources of pesticide pollution in surface waters. Since the point sources of pesticide pollution do not incorporate complex spread and transportation mechanisms throughout the environment, the sources of point pressures are much more identifiable compared to the nonpoint sources, which typically do not have a specific discharge location. On the other hand, it is relatively difficult to interpret and carry out clear source identification for diffuse pollution sources of pesticides, which involve agricultural activities as a primary source of pesticide pollution. Therefore, in literature, researches on the identification of diffuse pesticide pollution sources are not prevalent compared to the investigations conducted for the determination of point sources of pesticide pollution. In this thesis, as a primary diffuse source, the agricultural activities in the boundaries of the Yeşilırmak River Basin were addressed by sticking to the comprehensive data analysis, versatile assessment, and detailed source identification approach.

3.2.1 Impact of Crop Types and Locality of Farmlands on Pesticide Uses

The type and amount of the pests that occur in agricultural lands considerably change depending on the crop types. The agricultural crops can be a host for the different kinds of pests with their specific biological and chemical features. In this regard, the different types of crops are exposed to the different types of fungal diseases, weeds, and insects. While certain types of crops are susceptible to the various types of pests and require frequent spraying by pesticides, some of the crop types can have high resistance to the pests and do not require any pesticide usages. Hence, the type and dose of the pesticides applied on the different crop types are typically different. In this respect, it can be concluded that the contribution degree of pesticides to river pollution strongly depends on the type of the cultivated crops, which determine the type and abundance of pests. Therefore, pesticide pollution sources should be investigated by evaluating each crop type separately.

The location of agricultural activities is another substantial factor that directly influences the type and amount of pesticide usage, and consequently, the degree of pesticide pollution in the river. Regarding spatial variability of agricultural activities, different localities have different agricultural issues. The factors like climate, geography, soil type, and topography, which determine the type of plant diseases, insects, and other crop disrupters, can considerably change depending on the location of the agricultural area. Regarding the degree of the impact of locality on agricultural activities in the Yeşilırmak River Basin, the agricultural profiles in the basin typically show variability at the district scale rather than the province scale. The different districts located in the same province can have considerably different pesticide usage profiles since one province can comprise various microclimates belonging to different districts. As a result, it can be concluded that pesticide usage pattern changes considerably depending on region; thus, pesticide contamination should be analyzed and evaluated to the extent of small localities that represent a specific agricultural pattern. Within the boundaries of the Yeşilırmak River Basin, the agricultural lands of each of the districts and provinces are exposed to the different types and amounts of pests for the same type of crops due to the different rain regimes, temperature, elevation, and humidity. Thus, within the scope of this thesis, the assessment and examination of the agricultural profiles and pesticide usage trends were performed separately for each of the districts or provinces in the basin by following the district and province oriented analysis approach.

3.2.2 The Fate of Pesticides from Agricultural Fields to the Freshwater Environment

The extent of agriculture-based pesticide pollution present in the freshwater environment depends on various factors like agricultural land use patterns, irrigation strategies, physicochemical characteristics of the sprayed pesticides, and the localized climate, geography, and topography of territories where farming activities are carried out. After the application of pesticides in agricultural fields, pesticides are conveyed into river bodies by following different pathways. Spray drift, volatilization, surface runoff, soil erosion, and atmospheric deposition are the major entrance mechanisms of pesticides into the river bodies (Glinski, Purucker, Meter, Black, & Henderson, 2018; Brianda, Bertranda, Seuxa, & Millet, 2002). Glinski et al. (2018) stated that spray drift leads to the spread of pesticides by wind effect during pesticide application on agricultural fields. Spray drift carries pesticides from the target agricultural lands to the non-target environments. Volatilization and atmospheric deposition are other mechanisms that trigger the transportation of pesticides from agricultural areas to the freshwater environment. Volatilization of pesticides from agricultural fields can occur at different levels depending on the physicochemical properties of pesticides and climatic factors like temperature and humidity. According to Lenoir et al. (1999), the volatilization mechanism has the capacity to transport up to 90% of the sprayed pesticides from agricultural sites to non-target areas within a short period of time after application under certain conditions. Among the above-mentioned transportation mechanisms of pesticides, surface runoff is the most effective force that can severely drift pesticides from application zones to the freshwater environment. Richard et al. (1993) and Derbalah et al. (2003) emphasize that surface runoff is a fundamental force for the movement of pesticides from agricultural fields to freshwater environments. Surface runoff occurs under the effect of rain events, which wash the sprayed pesticides and drift them to the different environmental compartments. Duration and intensity of rainfall, land slope, and permeability of soil are major factors that significantly determine the degree of surface runoff. Purdue Pesticide Programs (PPP) (1995) stated that if soil binding strength (soil sorption capacity) of a pesticide is not strong enough then, pesticide entrance into freshwaters from application lands can happen in a few minutes or hours right after an intense rainfall event. In this regard, it can be understood that the duration between the time of pesticide application and time of pesticide occurrence within the river basin can be notably short, even in minutes if driving forces and environmental conditions are sufficient to trigger pesticide movement. When the combination of volatilization, rainfall events, spray drift, and other driving forces are taken into account, it can be concluded that pesticide transport from application fields can quickly happen within a short period of time regardless of driving force intensity. This thesis has paid particular attention to the analysis of the relation between the pesticide application months specific to each district and the pesticide observation months at the sampling stations of the corresponding districts within the Yeşilırmak River Basin by taking into account the impact of the timing and amount of precipitation events.

3.2.3 Impact of Physicochemical Characteristics of Pesticides on Pesticide Occurrence in the Freshwater Environment

In addition to external factors like precipitation, the physicochemical properties of pesticides also substantially determine the amount and the existence period of pesticides in the freshwater environment. Mobility and persistence are two significant pesticide characteristics that control pesticide spread, transportation, and overall behavior throughout their pathway to the freshwater. The soil sorption coefficient (Koc) and water solubility of a pesticide give information about pesticide mobility. Pesticides having high soil sorption capacity can strongly bind to soil; consequently, the movement of these pesticides from their existing position to different locations is relatively low compared to the pesticides having low soil sorption capacity. However, the transportation and dissemination of these pesticides to non-target environments are still inevitable since other mechanisms like soil erosion have a significant impact to convey these pesticides to different sites regardless of their strong soil attachment capability (Purdue Pesticide Programs, 1995). Solubility, which is related to the degree of dissolution in water, is another factor that affects the mobility of pesticides in the environment. Pesticides having moderate and high solubility are prone to maintain their existence longer in the freshwater environment. Moreover, high solubility brings about faster volatilization from the application field. However, compared to the properties of soil sorption capacity and environmental half-life, the solubility is less effective for the pesticide runoff mechanism. When environmental persistence is taken into account, soil and water half-lives of pesticides are the main indicators of pesticide persistence in the environment. The higher water and soil half-lives imply longer maintenance of pesticides in water and soil environments, respectively (Joint FAO/IAEA Division, 2018).

All in all, the soil sorption capacities and half-lives of pesticides are substantial factors that need to be taken into consideration during the assessment of pesticide occurrence in the freshwater environment. Pesticides having high soil sorption capacity and short half-lives in water and soil are expected to be observed in the freshwater environment in a short period of time after their application on the target sites. In this respect, the persistence and mobility of pesticides have critical importance for the identification of the relation between the periods of pesticide observations in the river and the periods of pesticide usage schedules of the farmlands. Therefore, this thesis was also taken into account the impact of the soil sorption capacities and soil and water half-lives of individual pesticides on the pesticide observations in the Yeşilırmak River Basin.

3.3 Methodology

3.3.1 Data Compilation and Analysis, and Selection of the Basin Specific Pesticides

The water quality data of the Yeşilırmak River Basin, which were collected within the context of the "Management of Point and Diffuse Pollutant Sources in the Yeşilırmak River Basin" project (Project Code: 115Y013), encompass the concentration data of 300 chemicals/pollutants. The monitoring data comprise the water quality measurement results of sampling every three months over a two year period. The water quality measurement stations are located within the boundaries of the eight provinces of the Yeşilırmak River Basin, which encompass Gümüşhane, Giresun, Sivas, Tokat, Amasya, Çorum, Yozgat and Samsun. These eight provinces embody 26 districts that locate 42 water quality measurement stations within their boundaries. Within the scope of this thesis, the pesticide concentration data of the 42 sampling stations were compiled and analyzed for the assessment and identification of the pesticide pollution observed at the sampling stations of the corresponding districts. As part of the data compilation; among the 300 chemicals reported in the monitoring results, 179 chemicals were identified as pesticide type pollutants, which consist of various insecticides, herbicides and fungicides. The concentration data of each of the 179 pesticides were analyzed and these 179 pesticides were prescreened for the selection of the basin-specific pesticides. For the purpose of prescreening, the pesticides whose dataset is composed of entirely below-LOD detections (100% of the data below LOD) were eliminated from the list of 179 pesticides. The datasets of the remaining pesticides were also prescreened by identifying the exceedances of their AA-EQS and MAC-EQS values. The exceedance of at least one of the MAC-EQS or AA-EQS values was determined as the pesticide selection criteria for the further assessments of the identification of the district-specific pesticide pollution sources. As a result of the selection, the pesticides that exceeded at least one of their AA-EQS and MAC-EQS values were identified for each of the districts that locates the corresponding sampling stations within their boundaries. The datasets of the selected pesticides were analyzed and examined individually within the context of the further assessments including district-specific source identification and general analysis of the temporal and spatial occurrence trends of the pesticides across the river basin.

3.3.2 Assessment of Spatial Distribution of the Pesticide Pollution Across the River Basin

In this part, it was aimed to analyze and determine the spatial distribution pattern of the pesticide pollution across the Yeşilırmak River Basin before proceeding with the district-based investigations. Within the scope of the district-based source identification, the agricultural activities were focused as the primary source of the pesticide pollution observed at the sampling stations of the river basin. Before starting a detailed examination of the district-specific agricultural sources of pesticide pollution, it was aimed to determine whether the agricultural activities in the basin are predominantly responsible for pesticide pollution compared to the other sources of pesticide pollution in the basin. In this respect, the compatibility between the spatial distribution of the agricultural areas across the basin and the spatial distribution of the pesticide occurrences throughout the basin was analyzed and assessed by taking into account the pesticide detection frequencies at the sampling stations located within the boundaries of the corresponding agricultural areas.

Within the context of the analysis of the spatial distribution of pesticide pollution, the major factors that have a high potential to affect the dissemination of pesticides throughout the basin were integrated into the assessment. The most effective factors that orient the runoff and transportation mechanisms of the pesticides from their application site to the river environment are the localized climatic conditions and geographic characteristics of the target site and physicochemical properties of the concerning pesticides.

In this respect, the relation between the persistence of 16 pesticides and their detection frequencies across the river were examined in order to figure out whether pesticide occurrences were originated from recent agricultural activities or historical agricultural activities. Since the persistence of the pesticides both in soil and water has critical importance for the spread pattern of the pesticides, both soil and water half-lives of the pesticides were taken into account to compare the trend of pesticide detections across the basin. All in all, the impact of water and soil half-lives on the detection frequency trend of the pesticides throughout the basin was analyzed in order to compare the occurrence frequency of persistent and nonpersistent pesticides across the river basin.

The mobility of pesticides is another significant factor that affects the occurrence and spread of pesticides throughout river bodies. The pesticides observed could originate from the nearby agricultural fields or remote agricultural areas by transportation over long distances. In order to fulfill reliable source identification of the pesticides, the extent of the mobility of the pesticides should be taken into account since the sources of the pesticides can be based on the pesticide spraying activities performed in remote agricultural areas rather than the surrounding environment of the polluted site. In this sense, the source identification analysis within the boundaries of the districts in the Yeşilırmak River Basin where the sampling stations measure the pollution would be unrealistic if the target pesticides are highly mobile and transported from remote areas. Therefore, before going into the district-specific source identification assessments, the mobility of each of the 16 pesticides was analyzed, and the relation of their mobility and detection frequency across the basin was examined. For this purpose, the soil sorption coefficient of each pesticide, which is a measure of mobility, was assessed by comparing the spatial distribution of the pesticides across the basin and their mobilities in the environment.

The data of soil sorption coefficients, water half-lives, and soil half-lives for the 16 pesticides were obtained from various sources, including the Pesticide Properties Database (University of Hertfordshire, 2020), US National Pesticide Information Centre (NPIC, 2019), Pesticide Action Network (PAN, 2019), Extoxnet Pesticide Information Profiles (Extoxnet, 2019) and the literature.

Geography is another substantial factor that has an impact on the agricultural profiles of the districts in parallel with pesticide usage schedules. District altitude, which is one of the major components of district-specific geographical characteristics, determines the local climatic conditions and the availability of the lands for agricultural activities. The change in altitude leads to the change in the type of pests that invade agricultural crops. Therefore, the diversity of pesticide types is generally expected to decline with the increase in the district altitude of the polluted site. In order to analyze this relation for the case of the pesticide pollution in the Yeşilırmak River Basin, the correlation between the altitude of each district and the diversity of the pesticide types detected at the sampling stations of the corresponding district was analyzed and assessed within the context of the spatial distribution evaluations of the 16 pesticides.

3.3.3 Assessment of Temporal Occurrence Trend of the Pesticide Pollution Across the River Basin

The temporal occurrence pattern of the pesticides in the river basin considerably depends on the timing of the pest infestations, which occur in specific periods for each crop type raised in the agricultural lands of each district in the river basin. Within the scope of this section, the time-dependent distribution of the pesticides across the river basin was analyzed in order to determine the basin-wide temporal occurrence profile of the pesticide pollution. In this regard, the observation months of the pesticide concentrations above their EQS values were identified for each of the sampling stations. The months that are responsible for the most frequent pesticide occurrences in the river basin were identified for the insecticide, herbicide, and fungicide observations.

Precipitation plays a functional role by triggering the runoff and spread of the pesticides from their application sites to the freshwater environment. In this respect, the precipitation trend across the river basin was identified by calculating the average of monthly precipitation amounts of the Gümüşhane, Giresun, Sivas, Yozgat, Tokat, Amasya, Çorum, and Samsun provinces where the water quality sampling stations are located, unlike for the other provinces of the river basin. The precipitation data of these eight provinces were obtained from the Turkish State Meteorological Service (TSMS). The monthly precipitation amounts of the particular region of the basin, which represent the average precipitation within the eight provinces the boundaries' were compared to the pesticide detections observed at the corresponding months. In this context, the impact of the precipitation events on the wash and spread of the sprayed pesticides were also evaluated by analyzing the frequencies of the pesticide occurrences above their EQS values.

3.3.4 District-Specific Identification of the Agricultural Sources for 16 Pesticides

For the achievement of the target-oriented source identification of the pesticide pollution observed in the river basin, the localized geographic and climatic conditions, which create a terrain-specific agricultural profile, should be taken into account individually for each of the districts. In order to fulfill this goal, first of all, the information on the type, spraying frequency, and spraying timing of the agrochemicals against the district-specific and crop-specific pests was obtained by individually contacting the agricultural engineers of the District Directorates of Agriculture and Forestry of the 26 districts that locate water quality sampling stations in their boundaries. Within the light of the site-oriented expert knowledge regarding district-based agricultural practices, the elaborative and detailed investigation was performed by gathering and compiling information on district-specific agricultural characteristics and the localized and time-integrated insecticide, herbicide and fungicide usage schedules of each crop type raised in each district. In this context, the comprehensive and detailed inventories, which encompass insecticide, herbicide, and fungicide spraying schedules of each crop type and typical agricultural practices, were prepared for each district where sampling stations are located. These district-specific inventories were used as the baseline for the identification of the pesticide pollution in the river basin. Furthermore, Corine 2018 agricultural land use data for the provinces located within the boundaries of the Yeşilırmak River Basin were examined in order to observe the exact distance between the agricultural field of each crop raised in each district and the water quality sampling stations located in corresponding districts. In this respect, the water quality sampling stations and

Corine 2018 land use data were integrated into the Yeşilırmak River Basin map in order to depict the general distribution of the agricultural lands throughout the river basin, which is provided in Figure 3.1. However, as it can be seen in Figure 3.1, Corine 2018 agricultural land use data enable a general overview of the spatial distribution of agricultural lands across the basin without specifying the type of the agricultural crops. More specifically, the Corine 2018 land use map provides only the location data of the major land cover groups like arable lands, fruit trees, and pastures rather than the crop-specific sub-groups like apple trees, tomato fields, etc. In order to accomplish elaborative and precise identification of the agricultural sources of pesticide pollution, each type of agricultural crop should be evaluated separately because the application period of the pesticides considerably differs for the different types of crops. Since Corine 2018 land use map only provides a general overview about the distribution of agricultural lands rather than crop-specific detailed data, within the context of this thesis, Corine 2018 land use data were not involved in the source identification study. In this thesis, the source identification of the pesticide pollution was employed by assessing the insecticide, herbicide, and fungicide spraying schedules of each crop type of each district separately.

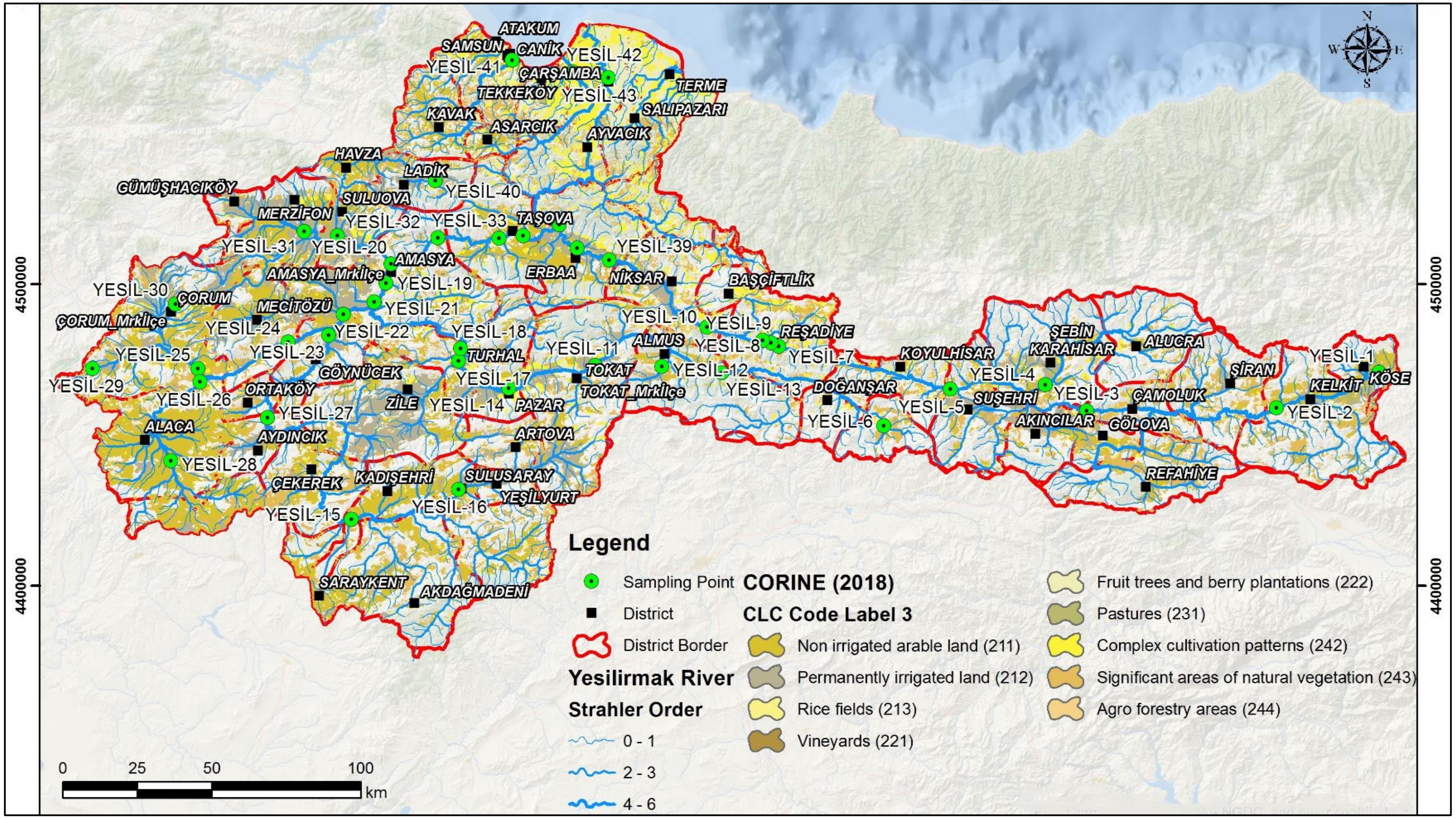

Figure 3.1 Map of the Corine 2018 Agricultural Land Use and the Water Quality Sampling Stations within the Boundaries of the Yeşilırmak River Basin

As a preliminary step for the source identification of the pesticides, the determination of dominant crops was performed in order to identify the crops that have high potential to contribute to the pesticide pollution in each district. The agricultural sources of the pesticides observed at the sampling stations of each district will be selected among the pre-determined dominant crops; therefore, the dominant crops can be defined as the candidate crops to be a source of the pesticides detected at the sampling stations of each district. The contribution degree of the farmlands of each crop to the pesticide pollution depends on the size of the crop cultivation area, which determines the amount of agrochemical sprayed on the cropland; therefore, the percentages of the areal shares of each crop type raised in each district were calculated for the identification of the dominant crops. Since the abundance of the pests that attack the crops occupying large cultivation areas will be high, the crops that cover the large farming areas in the districts will be exposed to more intense agricultural protection practices compared to the crops covering the small farming area. In this regard, the dominant agricultural crops cultivated in each of the 26 districts were determined by calculating the percentage shares of the crop areas both among the areas of other types of crops raised in the host district and among the areas of the same crop types raised in the other districts of the basin. By taking into account these two percentages, the extent of the farming activities for each crop type is aimed to be determined both at the basin scale and district scale. For the calculation of the areal shares, the data of crop-based and district-specific agricultural areas were obtained from the Turkish Statistical Institute (Turkstat). The percentages of the areal shares of the crops at the basin scale and district scale were defined as the indication of the degree of their possible contribution to the agrochemical pollution in the river basin. In this context, the crops that have areal share above 5% in all types of total crop areas in the district and above 5% in the same type of crop areas in the other districts of the basin were determined as the dominant crops of the districts. The exceedance of 5% by at least one of these two percentages was determined as selection criteria for the dominant crop identification. After the selection of the dominant crops for each district, the type and pollution degree of the pesticides that exceeded their EQS values at the sampling stations of each district were analyzed and determined by following district-specific assessments. For the identification of the degree of district-based pesticide pollution, the pesticides that exceeded at least one of their MAC-EQS and AA-EQS values at the sampling stations located in the boundaries of each district were determined, and their detection frequencies at corresponding sampling stations were calculated for each district.

After the preparation of the inventories on district-specific agricultural profiles, the determination of the dominant crops, and the identification of the type and degree of pesticide pollution in the boundaries of the districts, the temporal correlations between the agricultural activities and the pesticide occurrences were established for each district. More specifically, the temporal correlation between the EQS exceedance months of each pesticide at sampling stations of each district, and the insecticide, herbicide, and fungicide spraying schedules of each of the pre-determined dominant crops raised in each district were analyzed and determined. Based on the analysis of temporal correlations established for each district, district-specific precipitation trends, and also physicochemical properties of each pesticide, the district-based and crop-specific agricultural sources of each pesticide observed at each sampling station in the Yeşilırmak River Basin were identified within the scope of this thesis.

3.4 Results and Discussion

3.4.1 Data Compilation and Selection of the Concerning Pesticides for the Further the Assessment of the Localized Source Identification

The water quality measurements of 300 chemicals in the Yeşilırmak River Basin encompass 179 pesticides, which are composed of various types of agrochemicals like insecticides, herbicides, and fungicides. First of all, 179 pesticides were prescreened in order to select and exclude the pesticides that do not require further analysis due to their low concentrations in the river basin. When the datasets of 179 pesticides were analyzed, it was determined that among 179 pesticides, the datasets of 75 pesticides consist of completely non-detect values, which means all observations are below their LOD values (100% of data below LOD). Thus, these 75 pesticides were eliminated from being possible basin-specific pesticides. The datasets of the remaining 104 pesticides were further analyzed by calculating their percent AA-EQS and MAC-EQS exceedances at each of the sampling stations. In this regard, the pesticides that exceeded at least one of their MAC-EQS and AA-EQS values were selected as basin-specific pesticides. The average and maximum concentrations of the pesticides for each sampling station and their EQS values are provided in Table 4.1 of Appendix A.

As a result of the analysis and examination of the pesticide concentration data at the 42 sampling stations of the river basin, it was determined that 16 pesticides exceeded at least one of their AA-EQS or MAC-EQS values in the river basin. The list of the selected 16 pesticides and their regulatory status in Turkey is given in Table 3.1. The agricultural source identification of the pesticide pollution was performed for these 16 pesticides, which pose a great deal of concern for the water quality of Yeşilırmak River Basin due to their elevated concentrations and frequent detections in the river basin. The calculated detection frequencies, the MAC-EQS and AA-EQS exceedance percentages of these pesticides at each of the sampling stations are presented and discussed within the scope of the district-specific source identification and assessment of pesticide pollution provided in Section 3.4.4.

Table 3.1 The Basin Specific Pesticides and Their Regulatory Status in Turkey

Type of Pesticide	**Pesticide Name**	**Regulatory Status (Official Gazette No: 29899, 2016)**
Insecticides (10)	Imidacloprid	Approved
	Diflubenzuron	Approved
	Dichlorvos	Banned
	4,4'-DDD	Banned
	Permethrin	Banned

Table 3.1 (cont'd)

Type of Pesticide	**Pesticide Name**	**Regulatory Status (Official Gazette No: 29899, 2016)**
	Fenpropathrin	Banned
	HCH	Banned
	Fenthion	Banned
	Prothiofos	Banned
	Chlorfenapyr	Banned
Herbicides (4)	Diflufenican	Approved
	Bifenox	Approved
	Aclonifen	Approved
	Ethalfluralin	Banned
Fungicides (2)	Fenpropimorph	Approved
	HCB	Banned

Among the 16 pesticides, the use and production of 10 pesticides presented in red color in Table 3.1 have been banned in Turkey according to the Annex-II and Annex-IV of the Turkish Food Codex Regulation on Maximum Residue Limits of Pesticides in Foodstuff (Official Gazette No: 29899, 2016) and the EU within the context of the EU Regulation on Plant Protection Products (1107/2009/EC). Even though the 10 pesticides out of the 16 pesticides have been banned in Turkey, the concentrations of all these 16 pesticides were determined as above their EQS values at the water quality sampling stations of the Yeşilırmak River Basin. Among the banned ten pesticides, HCH and HCB are under cover of persistent organic pollutants (POPs) list set by the Stockholm Convention, an international treaty for the elimination or restriction of the chemicals of POPs list (Stockholm Convention on Persistent Organic Pollutants, 2001). The elevated concentrations of the banned pesticides in the Yeşilırmak river indicate that there is ongoing unregistered pesticide use in the basin. Since, except for HCB and HCH, the remaining 14 pesticides are non-persistent in the environment, thus the existence of the banned pesticides in the river basin can not be attributed to the historical pesticide spraying activities. (The details about the environmental persistence of each of the 16 pesticides are analyzed and discussed in Section 3.4.2.2 and Section 3.4.2.3).

On the other side, the high concentrations of the approved pesticides in the river point out that there exists excessive agrochemical usage within the boundaries of the river basin. In order to control the agricultural applications of the six approved pesticides and to eliminate the usages of the 10 banned pesticides, the agricultural sources of these pesticides in the river basin should be identified by addressing target-specific assessments. In this respect, by assessing the agricultural profiles and agrochemical usage schedules of each district that embodies the water quality sampling stations in their boundaries, the district-based agricultural sources in the river basin were identified for these 16 pesticides in the following sections.

3.4.2 Spatial Distribution of Pesticides Across the Yeşilırmak River Basin

In this study, the spatial distribution of the pesticides across the river basin was analyzed and evaluated to give a general overview of the location-wise behavior of the pesticides throughout the river basin. The following issues were analyzed and assessed in determining the spatial distribution of pesticides in the river basin,

- The relation between the spatial distribution of the agricultural areas and the pesticide occurrence pathway across the river basin
- The impact of water and soil half-lives of 16 pesticides on their detection frequencies across the river basin
- The relation between the mobility of the 16 pesticides and their spatial distribution across the river basin
- The impact of district altitude on the diversity of the pesticide types observed at the sampling stations of each district

In the upcoming sections, the analysis and examination of each of these issues are addressed in detail.

3.4.2.1 Relation Between Spatial Distribution of the Agricultural Areas and Pesticide Occurrence Pathway Across the River Basin

The pesticide pollution observed in the river basin can have different origins like agricultural land use, livestock activities, the discharges of industrial and urban wastewater treatment plants. Among these sources, agricultural activities are typically prominent as a potential source of pesticide pollution since agrochemical usage is the primary practice of agricultural activities and comprises versatile implementations for the protection of crops against various types of pests. Even though agricultural activities have a major contribution to pesticide pollution by nature, the other type of sources may also have a considerable impact on pesticide pollution in the river environment. Depending on the target site, the contribution of the agricultural activities to the pesticide pollution in the river can be relatively dominant or limited compared to the other sources. Therefore, the degree of the relation (strong or weak) between the agricultural activities and the pesticide pollution observed in the river body should be determined before the investigation of the crop-specific agricultural sources of the pesticide pollution. In other words, as prior step before going into the detailed analysis of the agricultural source identification of the pesticide pollution, the relation between the pesticide occurrences and the agricultural land use in the river basin should be examined in order to clarify whether the pesticide pollution at the target site is predominantly associated with the agricultural activities or other types of pesticide pollution pressures in the river basin. In the following sections, the correlation between the pesticide spraying schedules for each crop type raised in each district and the pesticide detection periods at the corresponding districts will be established with district-based evaluations. In order to attribute the existence of the pesticide pollution in the river to the specific farming activities during the district-based evaluations, the compliance between the distribution of agricultural lands in the river basin and the spread of the pesticide pollution across the river basin should be verified as a prior step of the detailed source identification assessments. In this section, the relation between the agricultural areas of the provinces across the river basin and the pesticide pollution observed at the sampling stations of the corresponding provinces was assessed in order to determine whether this correlation is strong or weak throughout the river basin.

The relation between the spatial distribution of the agricultural areas of each province and the number of pesticide detections at the corresponding sampling stations of these provinces is provided in Figure 3.2. The agricultural area given in the figure for each province does not represent the total agricultural land in these provinces. Instead, these areas represent the agricultural areas located in the districts of the provinces that have sampling stations in their boundaries. As it is presented in Figure 3.2, it was determined that the sampling stations in Gümüşhane, Giresun, and Sivas provinces, which are located in the eastern part of the basin, have a notably low number of pesticide detections that exceeded their EQS values. When the sampling stations of the Tokat, Amasya, Çorum, and Samsun provinces, which are located in the western part of the basin, are taken into consideration, it was seen that the sampling stations belonging to these four provinces have a considerably high number of pesticide detections above their EQS values. As it can be clearly seen in Figure 3.2, the agricultural area trend is sharply increasing in the lands of the Tokat, Amasya, Çorum, and Samsun provinces compared to the agricultural land use in the Gümüşhane, Giresun, Sivas, and Yozgat provinces of the river basin. As can be depicted from Figure 3.2, with a sudden increase in the agricultural areas, the number of pesticides that exceeded their EQS values is also drastically increasing by following the compatible upward trend. The sampling stations located in the Tokat and Amasya provinces, which have the largest agricultural areas with 1687519 da and 1713899 da in the basin, respectively, have the highest pesticide detection frequencies compared to the sampling stations located in the other provinces. In this respect, it was determined that there is a consistent and compatible increasing trend between the spatial distribution of the agricultural land use in the basin and the frequency of the pesticide detections at the sampling stations of the basin. As a consequence, it was identified that there is a strong compliance between the spatial distribution of the agricultural activities performed in the provinces of the basin and the spatial distribution trend of the pesticide detections observed at the corresponding sampling stations of these provinces.

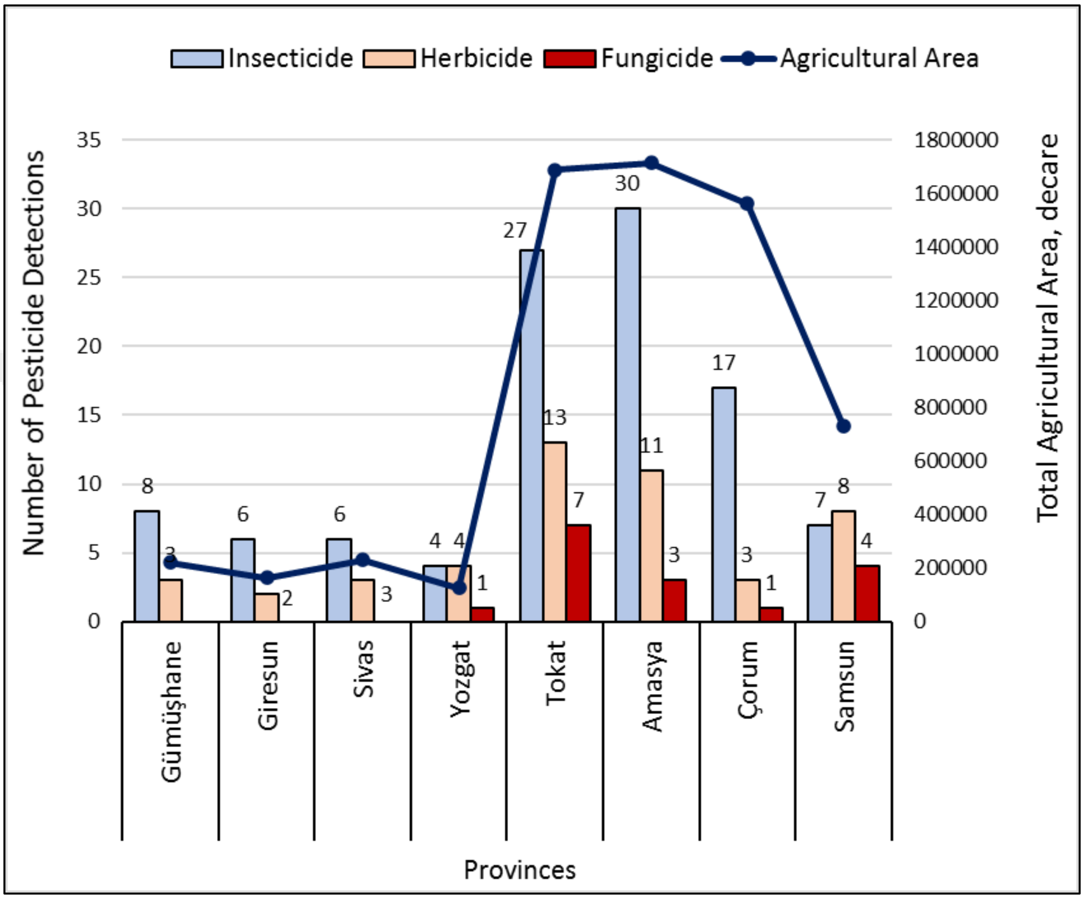

Figure 3.2 Spatial Distribution Relation Between Pesticide Detections and Agricultural Areas Across the River Basin

As it is shown in Figure 3.2, when the spatial distribution of the sub-groups of pesticides, which are insecticides, herbicides, and fungicides, are taken into account, it was seen that the insecticides and herbicides exceeded their EQS values in all provinces of the basin. As a result of their spatial distribution trend, the insecticides and herbicides were identified as widely spread agrochemical types of the river basin. On the other hand, the fungicides were not observed in the districts of all provinces that locate the sampling stations within their boundaries. As it is demonstrated in Figure 3.2, in the Gümüşhane, Giresun and Sivas provinces, where agricultural lands cover the smallest area compared to the other provinces, the concentrations of all fungicides were below their EQS values. The absence of the fungicide-type agrochemicals in these provinces points out that the provinces that embody relatively smaller agricultural areas have a lower diversity of pesticide types at their sampling stations. In the provinces, where agricultural lands occupy a relatively large area, both the detection frequencies of the pesticides and the diversity of the pesticide types are higher compared to the provinces, where agricultural lands are responsible for relatively small areas. In this regard, it was concluded that the spatial distribution of the agricultural land cover of the provinces across the basin is compatibly related to the number and diversity of the pesticides observed at the sampling stations of the corresponding provinces. This conclusion indicates that the agricultural activities performed in the basin are the key determinants for the spread of pesticide pollution across the basin compared to the other potential sources of pesticide pollution within the boundaries of the basin.

It should be noted that the absence of the fungicides at the sampling stations of the eastern provinces can also be associated with the impact of their high altitude topography, which prevents the existence of fungal diseases by favoring dry and cold climatic conditions. The impact of district altitude on agrochemical usage is discussed in Section 3.4.2.4, in detail.

3.4.2.2 Assessment of the Impact of Water and Soil Half-Lives of 16 Pesticides on Their Detection Frequencies Across the River Basin

The main focus of this section is to figure out whether the pesticide pollution observed at the sampling stations are originated from the historical applications or recent applications of the agricultural activities in the river basin. The occurrence of pesticides that have rapid degradation characteristics in the environment is likely to be the potential outcome of the recent spraying activities of pesticides. Whereas, the occurrence of the pesticides that have high persistence in the environment can be attributed to both recent and historical pesticide usage activities since their degradation and disappearance in the environment require a long period of time. The environmental half-life, which is a measure of persistence in the environment, is the main factor that determines how long pesticides can maintain their existence in the environment. In the upcoming sections of this thesis, the recent agricultural profile and the agrochemical usage trends of each district will be assessed for the identification of pesticide pollution sources. However, in order to ignore the impacts of historical agricultural practices on the current pesticide pollution trend and to focus only on the effects of the recent agricultural activities, the distinction between the contribution of historical and recent pesticide usage activities to the currently observed pesticide pollution should be clarified by assessing the physicochemical behavior of each of the 16 pesticides in the environment. In this regard, the environmental persistence of each pesticide should be taken into account while assessing the potential sources of pesticide pollution in the river basin. For this purpose, the impact of the environmental half-lives of the 16 pesticides on their occurrence in the river basin was analyzed and evaluated within the scope of this section. It was also aimed to reveal whether there exists a relation between the persistence of the pesticides and their detection frequency across the basin or not. Since agrochemicals are typically sprayed on agricultural crops, crop seeds or bare soil, they can maintain their existence both in the soil, where they are applied, and in the surface water, where they are transported from their application site. In this respect, both of the soil and water half-lives of the 16 pesticides were taken into account within the context of the assessments in this section. The data of water half-lives and soil half-lives for the 16 pesticides were obtained from Pesticide Properties Database (University of Hertfordshire, 2020), US National Pesticide Information Centre (NPIC, 2019), Pesticide Action Network (PAN, 2019) and Extoxnet Pesticide Information Profiles (Extoxnet, 2019).

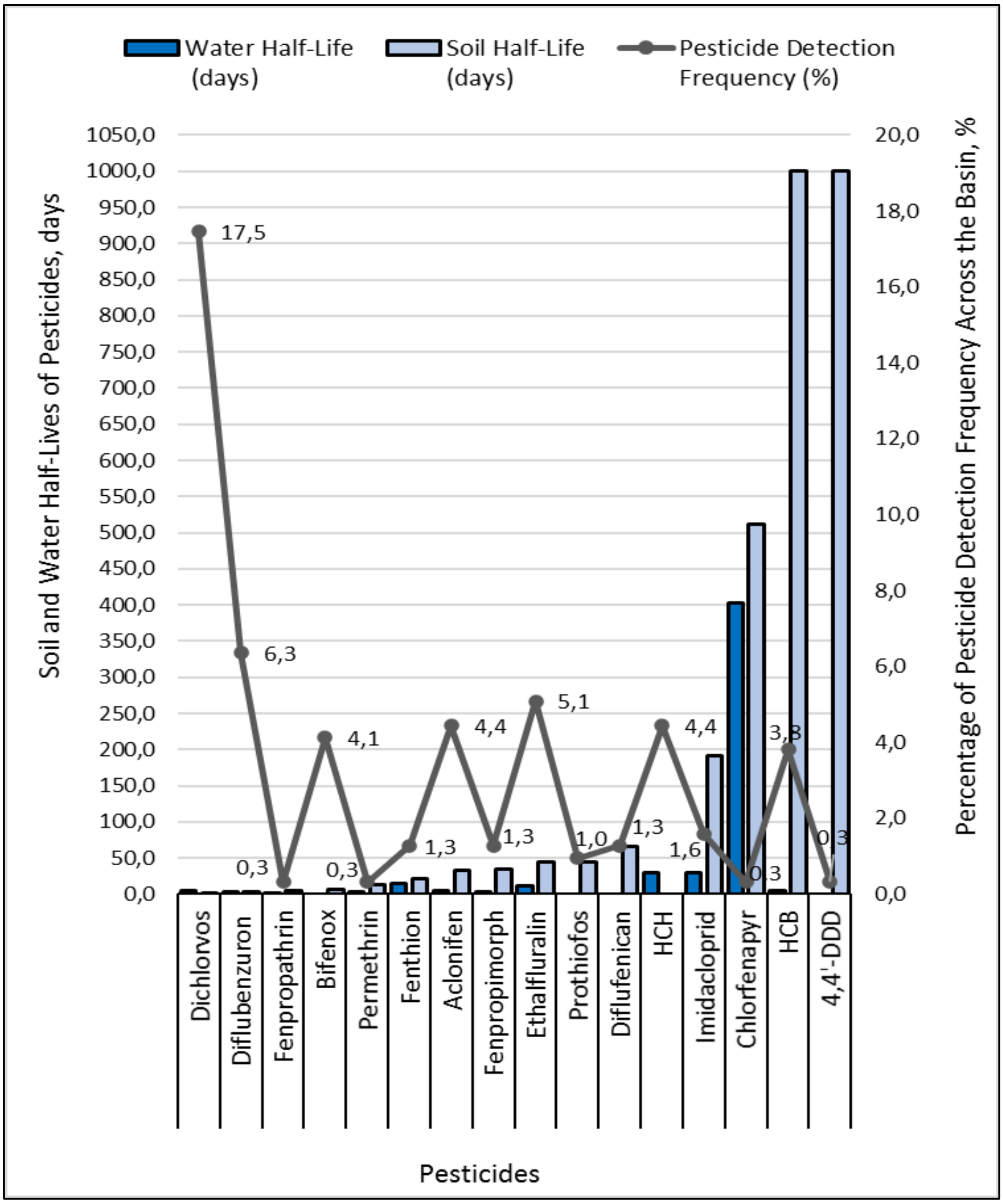

Figure 3.3 Water and Soil Half-Lives of the 16 Pesticides and Their Detection Frequencies Across the Basin

In Figure 3.3, the relation between the detection frequencies of the 16 pesticides throughout the basin and the soil and water half-lives of these pesticides was assessed in order to determine whether there is a correlation between the persistence of the pesticides and their observation frequencies. As it is provided in Figure 3.3, it was determined that among the 16 pesticides, dichlorvos, which has the highest detection frequency across the basin with 17.5%, has water and soil half-lives of four days and two days, respectively. Diflubenzuron, which was determined as having the second highest detection frequency with 6.3% after dichlorvos, has three days water half-life and three days soil half-life. All in all, dichlorvos and diflubenzuron were determined as the most frequently detected pesticides of the basin; on the other hand, their half-lives in water and soil are all less than four days. The high detection frequencies of dichlorvos and diflubenzuron in the river basin despite their nonpersistent characteristics in soil and water indicate that they currently have active spraying applications within the boundaries of the river basin. When the water half-lives of all 16 pesticides were examined, it was seen that except chlorfenapyr, the remaining 15 pesticides have water half-life below 30 days. In this regard, it was revealed that almost all of the pesticides observed in the basin can be rapidly degraded right after they reach to the river. When the soil half-lives of the 16 pesticides were evaluated, it was revealed that except chlorfenapyr, HCB, imidacloprid and 4,4'-DDD, all 12 pesticides have soil half-lives less than 50 days. Chlorfenapyr, HCB, imidacloprid and 4,4'-DDD, which are four exceptions by having persistent properties in soil among the other observed pesticides, were determined as having low detection frequencies across the basin as 0.3%, 3.8%, 1.6% and 0.3%, respectively. Even though chlorfenapyr, HCB, imidacloprid and 4,4'-DDD are nonpersistent in water, the occurrence of these four pesticides in the river can be originated from both recent and historical agrochemical implementations due to their persistent characteristic in soil. Except chlorfenapyr, HCB, imidacloprid and 4,4'-DDD, the remaining 12 pesticides have nonpersistent characteristics in the soil and in the river environment as a result of their short life time both in soil and water. In this context, it was concluded that the occurrence of these 12 pesticides in the river is likely to be originated from the recent pesticide usage activities rather than past pesticide applications since the common trait of all these 12 pesticides is their quick degradation both in the water and soil environment.

All in all, in this section, it was determined that the contribution of the recent pesticide spraying activities to the occurrence of the 16 pesticides in the river is predominant compared to the contribution of historical pesticide spraying activities performed in the river basin. In the upcoming sections, the source identification of these 16 pesticides carried out by following the assessment of the recent agrochemical usage trends of the districts of the river basin, are presented.

3.4.2.3 Assessment of the Relation Between the Mobility of the 16 Pesticides and Their Spatial Distribution Across the River Basin

In this section, the spatial distribution of each of the 16 pesticides across the basin was identified by assessing the impact of the pesticide mobility on the observed pattern of these pesticides throughout the basin. The soil sorption coefficient (Koc), which is the measure of soil binding tendency of chemicals, is the main parameter that determines the mobility of pesticides in the environment. There is an inverse relation between Koc value and pesticide mobility. High Koc value is the indication of low mobility in the environment since a pesticide with high Koc can strongly attach onto soil particles and can not travel over long distances. Pesticides having high mobility can substantially dissipate over a wide area from their application site (Purdue Pesticide Programs, 1995; Stevenson, Baumann, & Jackman, 1997). In order to figure out whether the pesticide pollution at the target site is originated from the vicinity environment or remote areas by transportation, the mobility of pesticides should be taken into account during the investigation of the pesticide pollution sources. In this respect, the relation between the pesticide occurrences and the soil sorption characteristics of the pesticides were evaluated by analyzing the location-wise dissemination trend of each of the 16 pesticides across the river basin.

As it is given in Figure 3.4, dichlorvos, which exceeded its EQS values at 39 sampling stations out of the 42 sampling stations, has the widest spatial distribution among the other pesticides. These 39 sampling stations represent the water quality of the river within the boundaries of a broad range of provinces, which comprise

Tokat, Amasya, Çorum, Samsun, Sivas, Yozgat and Gümüşhane. Dichlorvos as being the most widely dispersed pesticide across the river basin is followed by diflubenzuron, ethalfluralin and aclonifen, which were observed at 20 stations, 16 stations and 14 stations, respectively. When Figure 3.4 is examined, it can be seen that the most clear indication of the highly dispersed distribution of dichlorvos is its remarkably low Koc value of 50, which implies a “very mobile” physicochemical characteristic (NPIC, 2019). Compared to the other 15 pesticides, dichlorvos was determined as the only pesticide that has high mobility. Since the mobility of dichlorvos is very high, it is fairly difficult to estimate whether its existence is originated from vicinity districts by transportation over long distances or from the host district that embodies water quality sampling stations. On the other hand, the upward Koc value trend of the other 15 pesticides given in Figure 3.4 shows that all these pesticides have Koc values above 800, which corresponds to low mobility or complete immobility (NPIC, 2019). When the spatial distribution of these 15 pesticides presented in Figure 3.4 is examined, it can be clearly seen that their dissemination across the river basin is notably limited to the low number of sampling stations compared to dichlorvos. In this regard, it was concluded that the relatively low spatial distribution of these 15 pesticides is strongly compatible with their immobile characteristics. Since 15 of the 16 pesticides have low mobility or immobile property in the environment, the detections of these 15 pesticides can be attributed to the nearby pesticide pollution sources located within the boundaries of the host district that embodies the corresponding sampling stations. In this respect, it was revealed that the 15 pesticides detected in the river are not prone to travel over long distances and to be transported from remote agricultural areas to the target site where the pesticide pollution is observed. In other words, the transportation of these pesticides from their application district to the other districts is not an expected pesticide behavior due to the immobile nature of these pesticides.

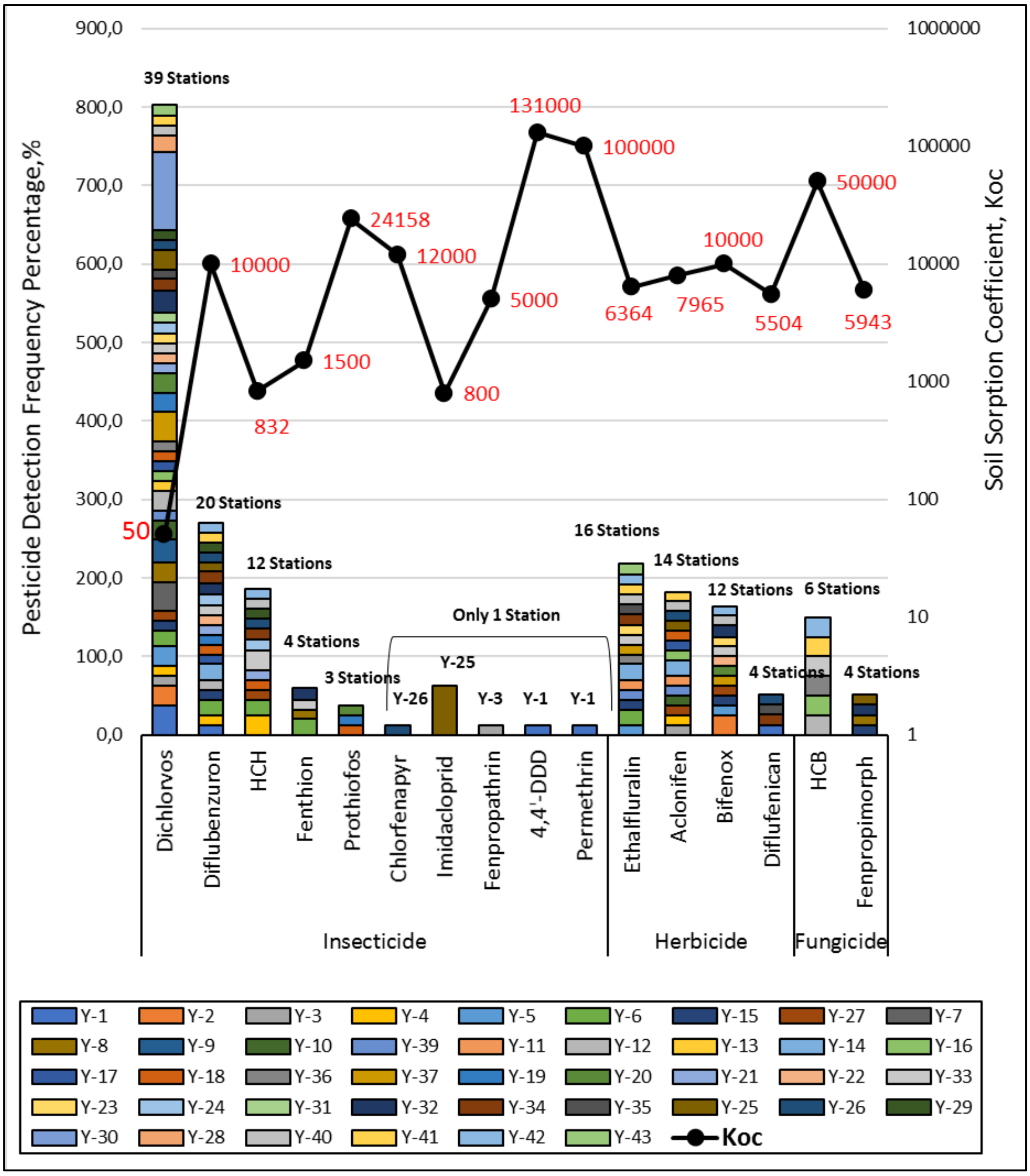

Figure 3.4 The Relation Between the Pesticide Detection Frequencies and the Soil Sorption Capacities of 16 Pesticides

The data of soil sorption coefficients for the 16 pesticides were obtained from Pesticide Properties Database (University of Hertfordshire, 2020), US National Pesticide Information Centre (NPIC, 2019), Pesticide Action Network (PAN, 2019) and Extoxnet Pesticide Information Profiles (Extoxnet, 2019).

Regarding the types of the pesticides detected in the river, as provided in Figure 3.4, insecticides were determined as the most widely observed pesticide type throughout the river basin. It was calculated that 10 insecticides, which are dichlorvos, diflubenzuron, HCH, fenthion, prothiofos, chlorfenapyr, imidacloprid, fenpropathrin, 4,4'-DDD and permethrin, exceeded at least one of their AA-EQS and MAC-EQS values in the Yeşilırmak River Basin. After insecticides, herbicides were identified as the second most observed pesticide type as having large spatial distribution across the river basin. Even though the herbicides were detected at a lower number of sampling stations compared to the insecticides, the herbicides were observed in all provinces of the river basin where water quality sampling stations are located. Unlike the insecticides and herbicides, the fungicides were observed at a limited number of sampling stations. All in all, the most widely distributed pesticide type of the basin was determined as insecticides, which is followed by herbicides and fungicides.

3.4.2.4 Relation Between Diversity of the Pesticide Types in Each District and Altitudes of the Corresponding Districts

The geographical characteristics of the districts play a crucial role in agricultural activities by determining the type of insects, weeds and fungal diseases that occur in the agricultural lands within the boundaries of the districts. District altitude is one of the most important geographical components that affect the type of pests occur in agricultural areas. In high altitude districts, fungal diseases and insect infestations generally do not occur in relation to the climatic outcomes of the high elevation. Whereas, low altitude districts provide favorable climatic conditions for the various types of pests to exist and attack agricultural areas (Hodkinson, 2005). In this section, the impact of the district altitudes on the diversity of the pesticide types observed at the sampling stations of the corresponding districts was analyzed as a part of the assessment of the occurrence of the 16 pesticides in the Yeşilırmak River Basin. The relation between the number of the pesticide types (diversity) observed at the sampling stations of each district and the altitudes of the corresponding districts of the river basin is presented in Figure 3.5. As it can be seen in Figure 3.5, it was determined that there is a negative correlation between the altitudes of the districts and the diversity of the pesticides observed at the sampling stations of the corresponding districts. In other words, it was revealed that the number of the pesticide types that exceeded their EQS values at the sampling stations of the districts decreases with the increase in district altitude. However, as it is depicted in Figure 3.5, this inverse relation trend is not consistent throughout the graph. More specifically, the inverse relationship between the abundance of the pesticide types detected at the sampling stations of each district and the altitude values of the corresponding districts is not valid for all districts of the river basin. These exceptions can be associated with the impact of the other district-specific factors like localized climatic conditions on the pest diversity in the agricultural lands and consequently, the diversity of the pesticide types observed in the river.

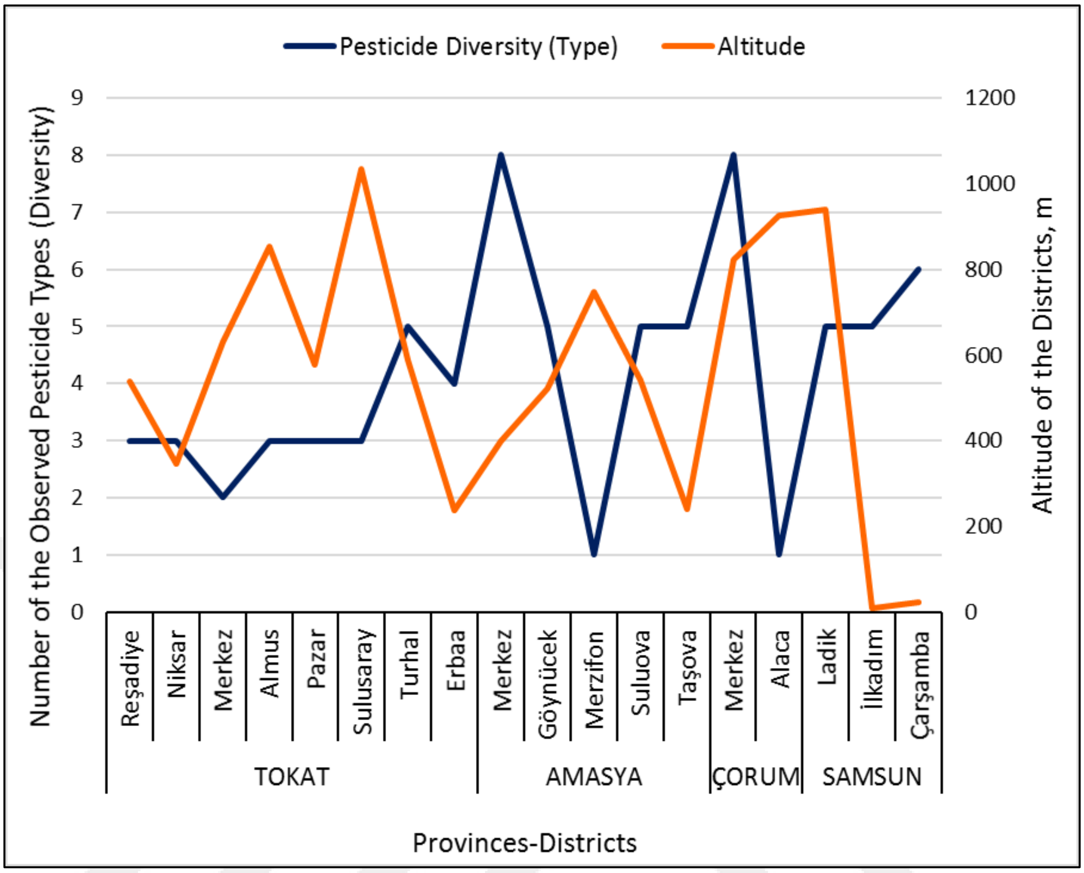

Figure 3.5 Relation Between Diversity of the Pesticide Types and Altitudes of the Districts

According to the results of the researches introduced by Ohsawa (1995) and Mallen-Cooper et al. (2008), high altitude regions suppress the living of variable specie types and abundance as a result of a decrease in temperature. Altitude changes create changes in species richness as a response to the weather changes like temperature and humidity, which have a substantial impact on the existence of the species (Ohsawa, 1995; Mallen-Cooper & Pickering, 2008). However, the results of the several studies that examined the relationship between the altitude and the variability of species showed that mid-altitudes could also be favorable for the living of the species rather than very low and very high altitudes (Gao & Liu, 2018). In the case of the Yeşilırmak River Basin, it was revealed that the decline in the altitude of the districts generally brings about the increase in the diversity of the pesticide types observed at the sampling stations of the districts. In parallel, this overall observation was associated with the increase in the diversity of the insects, fungal diseases and weeds that occupy the agricultural fields under the low altitudinal conditions.

3.4.3 Temporal Occurrence Trend of the Insecticide, Herbicide and Fungicide Pollution Across the River Basin

In this section, the time-dependent occurrence trend of the pesticides across the river basin was determined in order to reveal the basin-wide temporal occurrence profile of the pesticide pollution. In this context, the detection months of the insecticide, herbicide, and fungicide concentrations that are above their EQS values were identified for each of the sampling stations. As it is shown in Figure 3.6, the most widely dispersed insecticide pollution was observed in August. In the month of August, the EQS exceedances by insecticides were detected in 34 sampling stations of the river basin. Regarding herbicide pollution, April is the month of the highest occurrence of herbicide pollution in the river. In April, the concentrations of the herbicide-type pesticides were calculated as above their EQS values at 16 sampling stations of the river basin. When it comes to fungicide pollution, October was determined as being responsible for the widest fungicide occurrence across the river basin. In October, the concentrations of the fungicide-type pesticides were calculated as above their EQS values at six sampling stations of the basin. As it is demonstrated in Figure 3.6, in the months of January and February, only insecticide-type pesticides were determined as above their EQS values at the four and two sampling stations, respectively. Since the harsh climatic conditions in winter, which mainly occur in the months of December, January, and February, do not favor the existence of the pests in the agricultural fields, the abundance and diversity of pesticides in these two months were expected to be less compared to the other months.

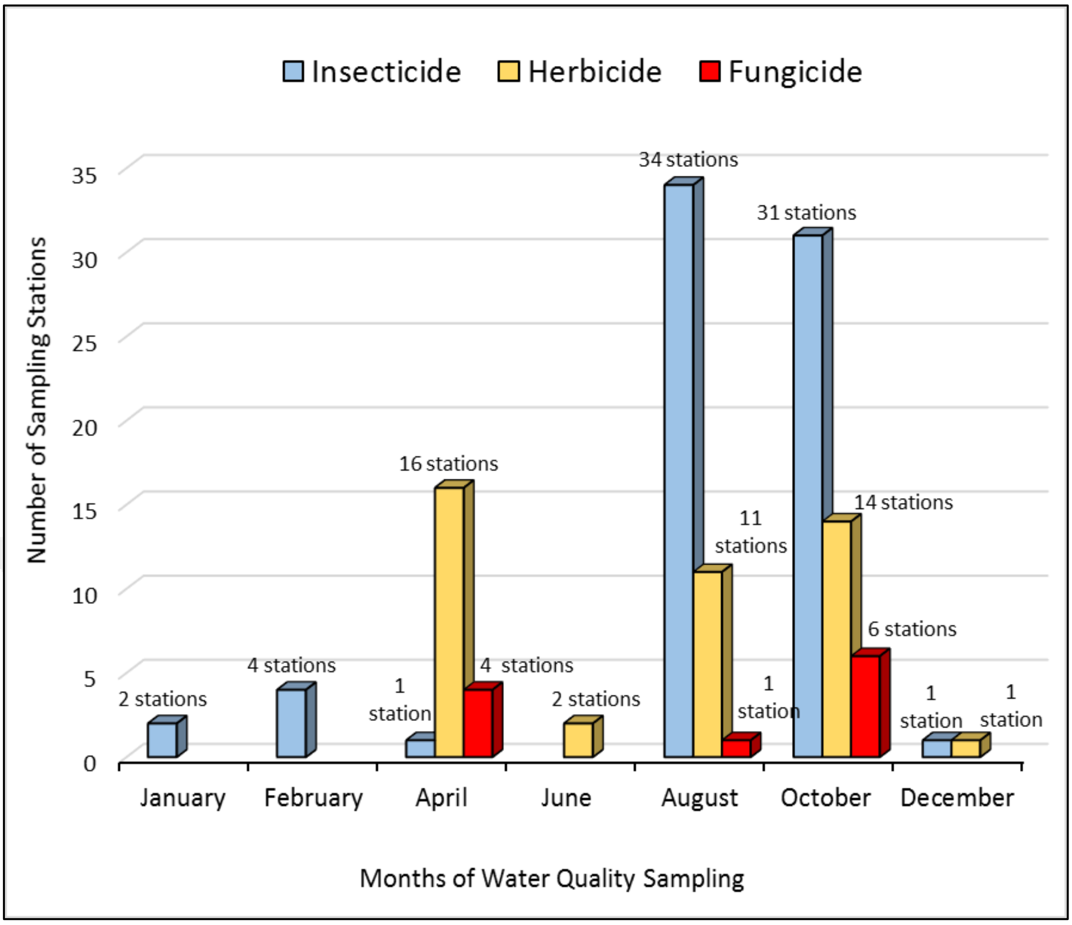

Figure 3.6 Temporal Occurrence Trend of Insecticide, Herbicide and Fungicide Pollution Across the River Basin

All in all, the most frequent and widespread occurrence of all insecticides, herbicides and fungicides across the river basin was observed in October. When the district-specific pesticide spraying schedules obtained from the agricultural engineers of District Directorates of Agriculture and Forestry in the river basin (2019), were examined and compared, it was revealed that the common trait of the pesticide spraying schedules of the districts of the basin is the period of the pesticide spraying activities for grain-type crops like wheat and barley. In general, October is the month of seed spraying for the wheat crops in most of the districts of the basin (Personal Communication with the Agricultural Engineers of District Directorates of Agriculture and Forestry , 2019). The grain fields within the boundaries of the river basin occupy the largest agricultural area compared to vegetables, fruit trees and other types of field crops. There is a large difference between the total cultivation area of grain fields and the area of other crop types raised in the districts of the river basin. For instance, the total area of tomato, apple, grape, onion, and tobacco within the boundaries of 26 districts of the river basin are 70933 da, 27973 da, 73385 da, 113811 da, and 21805 da, respectively. The total area of these crops is substantially smaller compared to the total grain area (2978045 da) in the basin (TurkStat, 2020). Even though the pesticide spraying periods considerably change depending on the district-specific agricultural profiles, the general pesticide spraying pattern of the grain fields is almost similar in most of the districts throughout the river basin. In this respect, since wheat fields are responsible for the largest agricultural lands of the basin and the seed spraying of wheat crops are performed all across the basin in October, the October observations of the pesticides were associated with the pesticide spraying activities of wheat crops in the river basin. The district-specific evaluations of the relation between the pesticide occurrence months and the pesticide spraying schedules of each crop type raised in each district are discussed within the scope of Section 3.4.4.

3.4.3.1 Temporal Relation Between Precipitation Trend and Pesticide Occurrence Trend in the River Basin

The precipitation amount is one of the most effective driving forces that triggers the transportation of pesticides by washing them from the application sites to the river basin. The assessment of the impacts of precipitation changes on the pesticide occurrences in the river basin is a critical step for the analysis of reliable pesticide source identification. In this respect, this section mainly focused on the relation between the basin-wide monthly detection frequencies of the pesticides and the monthly precipitation trend across the basin. For this purpose, the monthly average precipitation amount in the eight provinces of the basin where sampling stations are located was analyzed by using the province-based monthly precipitation data reported by the Turkish State Meteorological Service (2020).

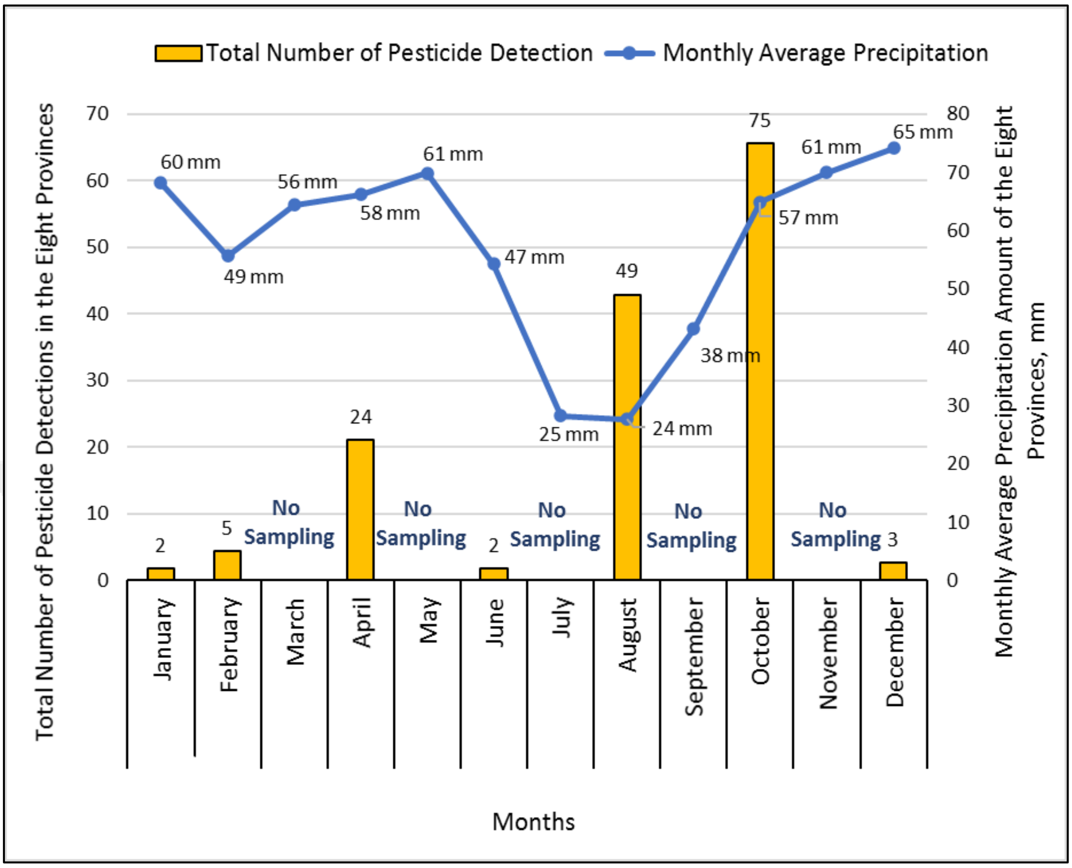

Figure 3.7 Relation Between Monthly Precipitation Pattern and Temporal Trend of Pesticide Detections in the River Basin

As it is shown in Figure 3.7, the highest frequency of the total pesticide detections throughout the river basin was observed in October. The average precipitation amount in the eight provinces of the basin was calculated as 57 mm in the month of October. As it can be seen in Figure 3.7, from August to October, there is a drastic upward trend in the precipitation amount, which is strongly parallel with the increase in the number of total pesticide detections. In this regard, it was determined that the most dramatic increase in the graph coincides with the highest pesticide detection in the river basin. On the other hand, despite the high precipitation amounts in December, January and February, the pesticide detections in these months were determined as considerably low in number. The low number of pesticide occurrences in these months was attributed to the dominance of snow-type precipitation, which is less effective to wash and transport the pesticides to the non-target sites, over rain-type precipitation in these months. For the effective washing force, the type of precipitation should be rain rather than snow. Therefore, the number of pesticide detections in the river was not expected to be high in the months of December, January, and February. As a result of these assessments, it was determined that the temporal precipitation trend of the river basin is generally compatible with the monthly occurrence trend of the pesticides in the river basin. This compatibility shows the active role of the precipitation factor as an effective driving force in the occurrence of the pesticides in the Yeşilırmak River Basin.

3.4.4 District-Specific Source Identification of Pesticide Pollution in the Yeşilırmak River Basin

The Yeşilırmak River Basin incorporates 8 provinces with 26 districts that embody water quality sampling stations within its boundaries. In this section, agricultural activities implemented in each of the 26 districts were assessed individually by taking into account the district-specific pest infestation periods of the farmlands and the application schedules of insecticides, herbicides, and fungicides for the pre-determined dominant crops of each district. Within the light of these assessments, the potential contribution of crop-specific farming activities to the observed pesticide pollution in each of the 26 districts were determined based on the correlation between the monthly pesticide usage schedules of each district and the observation months of the pesticides that exceeded their EQS values at the sampling stations of the corresponding districts. In the following sections, the agrochemical usage pattern of in districts of the basin will be assessed, and the sources of the pesticide pollution observed at the sampling stations of each district will be identified by following the comprehensive evaluation of the agricultural profiles, the topographic features and the climatic conditions of each district individually.

In the following sections, the results of the agricultural source identification study on pesticide pollution for the Gümüşhane, Giresun, Sivas, Tokat and Amasya

Provinces are presented. The results for the Samsun, Çorum and Yozgat Provinces are given in Appendix B, Appendix C, and Appendix D, respectively.

3.4.4.1 Gümüşhane Province

The Gümüşhane Province embodies the Y-1 and Y-2 sampling stations, which are located within the boundaries of the Köse District and the Kelkit District of the province, respectively. The Gümüşhane Province has an 1150 m altitude, which is the highest altitude compared to the altitudes of the other provinces of the basin. This high altitude of the province brings about a cold climate, which prevents the abundance of pest infestations in the farmlands of the province. The climate of the Gümüşhane Province is under the effect of both the Eastern Blacksea region and Eastern Anatolia region, which creates variable climatic conditions from district to district; thus, agricultural diversity in the districts of the province can be substantially different and independent from each other. Even though Köse and Kelkit are located in the same province, the abundance and diversity of agricultural cultivation in these two districts are different from each other. Hence, the contribution of agricultural activities in these districts to the pesticide pollution observed at the corresponding sampling stations of the river should be evaluated separately for each of the districts. In this regard, the assessments of the typical agricultural profile of Köse and Kelkit districts and the source identification of the pesticide pollution within the boundaries of these districts are performed in Section 3.4.4.1.1 and Section 3.4.4.1.2, respectively. Besides, in the above-mentioned sections, the analysis of the pesticide concentration data obtained from the Y-1 and Y-2 sampling stations will be carried out by involving the examination of the agrochemical applications for the farmlands in each of the districts.

3.4.4.1.1 Köse District (Y-1 Sampling Station)

The general characteristic of agricultural practices in Köse is mainly determined by the highly elevated topographical features of this district. According to the agricultural engineers of Köse District Directorate of Agriculture and Forestry (2019), the agricultural activities performed in this district are relatively low compared to the other districts of the Gümüşhane Province due to the existence of high altitude topography (1577 m) in Köse. Domination of mountainous areas in Köse creates a favorable environment for animal husbandry practices rather than agriculture. Since animal husbandry activities demand a large quantity of grains (wheat, barley etc.) for the usage as animal feed, grain fields cover large areas in the district (Personal Communication with the Agricultural Engineers of Köse District Directorate of Agriculture and Forestry, 2019). As it can be seen in Table 3.2, it was calculated that the total area of wheat, barley, alfalfa, and sainfoin, which are all animal feed grains, are responsible for 85% of the total agricultural land use in the Köse District. This high percentage proves that agriculture in the Köse District is fundamentally composed of grain cultivation, which serves as animal feed. The red-colored crops given in Table 3.2 represent the determined dominant crops of the Köse District, which have areal percentage share above 5% among the areas of all types of crops raised in the Köse District or areal percentage share above 5% among the same type of crop areas raised in the 26 districts of the basin. The exceedance of 5% by one of these two percentages of the crop area implies that the area of the crop has a considerably high areal share both at the basin scale and at the district scale, which is an indication of the high potential of the crops to contribute to the observed pesticide pollution.

Table 3.2 The Calculated Percentage Shares of the Crop Areas in the Köse District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Köse District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Wheat	34509	**53**	1.2
Barley	14397	**22**	1.8
Bean	7026	**10**	**12.2**
Alfalfa	4000	**6**	1.6
Sainfoin	3000	4	**6.3**
Potato	1000	2	2.3
Maize	400	1	0.1
Rye	240	0.4	**5.1**
Triticale	90	0.1	0.1
Other Crops	Negligibly Small Portion		

As it is provided in Table 3.2, wheat, which is the major member of grains, has the largest agricultural area compared to the other crops raised in the Köse District. Even though the wheat area in the Köse District has a low percentage share (1.2%) compared to the wheat areas cultivated in the other districts of the Yeşilırmak River Basin, the area of wheat compared to other crops raised in the boundaries of the Köse District has remarkably high percentage share (53%). The high percentage share of the wheat crop makes the wheat fields a major candidate for the source of the observed pesticide pollution within the boundaries of the Köse District. The wheat crop that is identified as the dominant crop of Köse is followed by barley, bean, alfalfa, sainfoin, and rye crops, which were all determined as having areal percentage shares higher than 5%. In this case, potato and maize were not taken as the dominant crops of Köse since their calculated percentage shares both at the basin scale and at the district scale were determined as below 5%. As a result of these evaluations for each of the individual crops raised in the Köse District, wheat, barley, bean, alfalfa, sainfoin, and rye were determined as the dominant crops of the Köse District in terms of their potential to contribute to the pesticide pollution.

3.4.4.1.1.1 Determination of the Potential Sources of Insecticide Pollution at the Y-1 Sampling Station of Köse

According to the agricultural engineers of the Köse District Directorate of Agriculture and Forestry (2019), the agricultural products raised in the Köse District typically are not exposed to the insect infestations since the altitude of the district is considerably high (1577 m), which limits abundancy and diversity of the insects in the district. Therefore, the insecticide usage is remarkably rare or not applied at all in the Köse District. For instance, the bean production requires a high amount of insecticide usage due to the infestation of bean crop-specific insects existing in many of the districts of the Yeşilırmak River Basin; however, in the Köse District, the insecticide spraying for the bean crop is not performed due to the absence of bean seed bugs. Moreover, the stink bug and wheat bug, which are the most common insect types of the grain farmlands, are not observed in the grain cultivation fields of the Köse District due to the effects of the high elevation of the district as in the case of the bean crop. All in all, the topographical characteristic of the Köse District eliminates the insecticide usage requirement of the farmlands of the district (Personal Communication with the Agricultural Engineers of Köse District Directorate of Agriculture and Forestry, 2019). In this respect, it can be understood that the regional topography has a significant impact on the agricultural spraying requirements of croplands of a district, as in the case of the Köse District.

As it is presented in Table 3.3, the concentrations of dichlorvos, 4,4'-DDD, permethrin and diflubenzuron insecticides were determined as above their EQS values at the Y-1 sampling station of the district. However, among these insecticides, only dichlorvos was determined as exceeding both of the AA-EQS and MAC-EQS values while 4,4'-DDD, permethrin, and diflubenzuron insecticides were determined as exceeding only their MAC-EQS values. AA-EQS and MAC-EQS exceedance percentages of dichlorvos were calculated as 5721% and 20933%, respectively. Compared to the other observed insecticides, dichlorvos has remarkably high EQS exceedance percentages. Moreover, the highest percentage of detection frequency, which was calculated as 37.5%, corresponding to three measurements out of eight sampling periods, also belongs to dichlorvos. On the other hand, 4,4'-DDD, permethrin, and diflubenzuron insecticides were determined as exceeding their EQS values only in one observation out of eight sampling periods.

Table 3.3 Potential Sources and Detection Percentages of the Insecticides Observed at the Y-1 Sampling Station of Köse

<table>
<tr><th rowspan="2">Stations</th><th rowspan="2">Insecticides</th><th colspan="2">EQS Exceedance, %</th><th rowspan="2">Detection Frequency %</th><th rowspan="2">Potential Sources of the Observed Insecticides</th></tr>
<tr><th>AA-EQS</th><th>MAC-EQS</th></tr>
<tr><td rowspan="4">Y-1</td><td>Dichlorvos</td><td>5721</td><td>20933</td><td>37.5</td><td rowspan="4">Agricultural Source:
- Not Exist
Industrial Source:
- Wastewater Discharges of the Animal Feed Industry</td></tr>
<tr><td>Diflubenzuron</td><td>-</td><td>6</td><td>12.5</td></tr>
<tr><td>Permethrin</td><td>-</td><td>350</td><td>12.5</td></tr>
<tr><td>4,4'-DDD</td><td>-</td><td>45</td><td>12.5</td></tr>
</table>

As it can be seen from the results given in Table 3.3, compared to other insecticides detected at the Y-1, dichlorvos has notably higher EQS exceedance levels and detection frequencies. These results indicate that dichlorvos poses a relatively greater concern to the insecticide pollution observed in the river environment within the boundaries of the Köse District compared to the 4,4'-DDD, permethrin, and diflubenzuron insecticides. On the other hand, as it was explained, it is not expected to have agricultural-based insecticide pollution within the boundaries of the Köse District since insecticide usage is not an agricultural practice in this district. The climate and topography of the district do not provide a favorable environment for insect infestations in the farmlands of the district. As it was stated by the agricultural engineers of Köse District Directorate of Agriculture and Forestry (2019), the wheat fields as being the dominant agricultural lands of the Köse District are not sprayed by insecticides since the wheat bugs are not existing in the Köse District. In this respect, it was revealed that there is a discrepancy between the existence of insecticide detections at the Y-1 sampling station and the absence of insecticide spraying activities of the farmlands in the Köse District; therefore, it was concluded that the insecticide pollution observed at the Y-1 sampling station is not related to the agricultural land use in the Köse District. On the other hand, even though it was figured out that the agricultural activities are not responsible for the insecticide pollution in the Köse District, the calculated EQS exceedances of the dichlorvos, permethrin, diflubenzuron, and 4,4'-DDD insecticides at the Y-1 sampling station indicate that there exist other insecticide pollution sources except the agricultural activities in the district. The certain type of industrial facilities located in the district can also be a potential source of the observed insecticide pollution. In this regard, the industries that integrate the insecticide usage into their process steps or use raw materials exposed to the agrochemicals were also taken into account as the potential source of the observed insecticide pollution. When the industries located within the boundaries of Köse are examined, it was identified that the animal feed facility (Ak-Can Animal Feed Production Industry) is the only industry that has high potential to be responsible for the observed pesticide pollution and discharges its wastewater into the Yeşilırmak River within the boundaries of the Köse District. The animal feed manufacture uses a wide range of raw materials, which are generally corn, sugarbeet pulp, soybean, sunflower, grains, waste vegetable oils, and byproducts of different food industries. The raw materials used in the animal feed industry are protected by different types of agrochemicals (Karakuş, 2017; Türkiye Yem Sanayicileri Birliği, 2019). The variability of the crops used as a raw material in this industry can be seen as the indication of high insecticide diversity detected at the Y-1 sampling station, which comprises four different types of insecticides, which are dichlorvos, 4,4'-DDD, permethrin, and diflubenzuron. Hence, it was revealed that the wastewater discharges of the animal feed industry located in the Köse District is likely to be responsible for the calculated EQS exceedances of the dichlorvos, 4,4'-DDD, permethrin and diflubenzuron insecticides. In this respect, the animal feed industry was identified as the potential source of the insecticide pollution observed at the Y-1 sampling station of the Köse District.

3.4.4.1.1.2 Determination of the Potential Sources of Herbicide Pollution at the Y-1 Sampling Station of Köse

In the Köse District, herbicides have a relatively higher spraying rate compared to fungicide and insecticide spraying activities of the farmlands in the district. The herbicides are typically applied before and after the cultivation of agricultural products. Before cultivation of the crops, the herbicides are sprayed directly on bare soil. By soil tilling practice, the soil that is sprayed with herbicides is mixed in order to blend and spread the herbicides throughout the soil (Personal Communication with the Agricultural Engineers of Köse District Directorate of Agriculture and Forestry, 2019). According to the agricultural engineers of Köse District Directorate of Agriculture and Forestry (2019), the spraying event that applied on the bare soil can highly contribute to the herbicide contamination in the river since the bare soil can sweep away the applied pesticides easier compared to the plants covered with the pesticide residues.

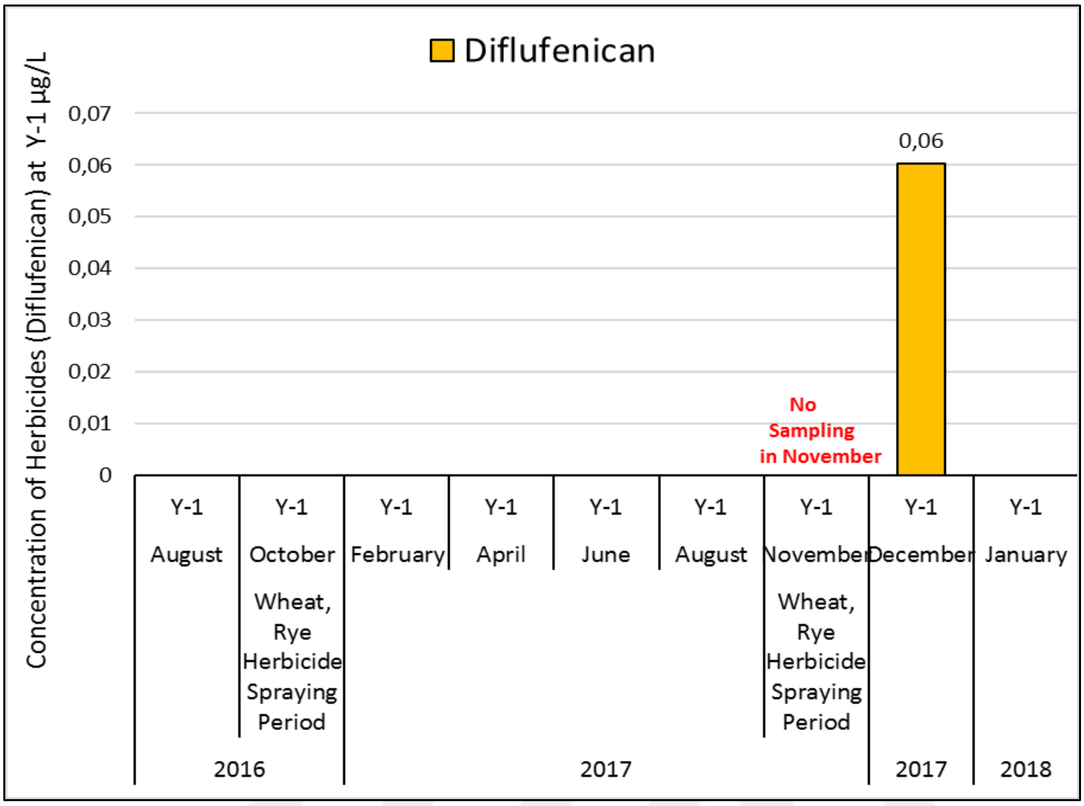

Figure 3.8 Correlation Between EQS Exceedance Months of Herbicides (at Y-1) and Herbicide Spraying Periods for the Dominant Crops of Köse

When the concentration data of the herbicides observed at the Y-1 sampling station were analyzed, it was determined that diflufenican is the only herbicide that exceeded its EQS values at the Y-1 sampling station. As it can be seen from Table 3.4, it was calculated that diflufenican exceeded both its AA-EQS and MAC-EQS values with 19% and 502%, respectively. As it is demonstrated in Figure 3.8, the EQS exceedances of diflufenican were observed only in November. When the dominant agricultural products of the Köse District are taken into account, as it was provided in Table 3.2, the wheat crop was determined as having the largest agricultural area (53% among entire crops) in the district. According to the herbicide spraying schedules of the dominant crops of the Köse District provided by the agricultural engineers of Köse District Directorate of Agriculture and Forestry (2019), the wheat crop is sprayed by herbicides in November in the Köse District. However, there is no water quality measurement performed in November at the river basin; therefore, the level of herbicide pollution in November is not available. On the other hand, the measurement results of December as being the following month of November provide the concentration data of herbicides at the Y-1 sampling station. When the measurement results in December were analyzed, it was calculated that the concentration of diflufenican is above both of its MAC-EQS and AA-EQS values this month. The elevated diflufenican concentration observed in December can be related to the herbicide spraying activities of the wheat crop, which is performed in November in the Köse District. Among the other dominant crops of the district, wheat is the only crop that is sprayed in November by herbicides. Since there is no herbicide spraying activity performed in December in Köse, the herbicide spraying of the wheat crop implemented in November is the only and major candidate as the source of the observed herbicide pollution. Moreover, when the impact of monthly precipitation amount in the Köse District on the observed herbicide pollution is taken into account, it was revealed that November and December have higher precipitation amounts compared to the previous months. According to the monthly precipitation data of the Köse District obtained from the Meteoblue historical climate database (2019), the monthly average precipitation of Köse has its lowest amount in July and August as 11 mm and 10 mm. After this drought season, the sudden increase in the precipitation amount occurs in November and December as 36 mm and 27 mm, respectively (Meteoblue Climate History in Köse , 2019). This drastic increase in the precipitation event can trigger herbicide runoff from the wheat fields to the river in November and December. In this respect, it was determined that the EQS exceedance period of diflufenican herbicide, the herbicide spraying schedule of wheat crop raised in Köse, and the temporal trend of the monthly precipitation amount of the district were all correlated with each other. All in all, diflufenican observations at the Y-1 sampling station of Köse in December sampling period strongly point out the herbicide spraying practices applied intensely in November in the wheat fields, which cover considerably large area by being responsible for 53% of the total agricultural land use in Köse. Hence, 34509 da wheat cropland of the district was determined as the potential source of the diflufenican pollution observed at the Y-1 sampling station of the district. Furthermore, as in the case of the insecticide pollution explained in Section 3.4.4.1.1.1, the wastewater discharge of the animal feed industry located in Köse was also identified as the potential source of the observed herbicide pollution.

Table 3.4 Potential Sources and Detection Percentages of the Herbicides Observed at the Y-1 Sampling Station of Köse

Stations	**Herbicides**	**EQS Exceedance, %**		**Detection Frequency %**	**Potential Sources of the Observed Herbicides**
		AA-EQS	**MAC-EQS**		
Y-1	Diflufenican	19	502	12.5	**Agricultural Source:** - Wheat Farmland: 34509 da **Industrial Source:** - Wastewater Discharges of the Animal Feed Industry

3.4.4.1.1.3 Determination of the Potential Sources of Fungicide Pollution at the Y-1 Sampling Station of Köse

In the Köse District, fungicide pollution was not observed at the Y-1 sampling station. When the fungicide usage profile of the district, which is provided by the agricultural engineers of the Köse District Directorate of Agriculture and Forestry (2019), was examined, it was revealed that the fungicides are commonly applied to the seeds of the field plants (wheat, barley etc.) before cultivation of the seeds in the Köse District. As a fungicide application technique, the preference of seed spraying rather than soil spraying and plant spraying provides the reduction of fungicide based agrochemical pollution in the aquatic environment. The amount of the fungicides used in the seed spraying is relatively low compared to the foliar spraying (spraying directly on the plant) and soil spraying techniques since the soil spraying and the plant spraying require greater application surface (Lamichhane, You, Laudinot, Barbetti, & Aubertot, 2020). Moreover, while the fungicides that are applied on soil or directly on the plant can disseminate over a large area, the fungicides that are sprayed on the seeds of the plants tend to remain on the seeds rather than drift to the non-target environment (Zubrod, et al., 2019; Lamichhane, You, Laudinot, Barbetti, & Aubertot, 2020). Thus, the usage of only seed spraying as a fungicide application technique on the field crops of Köse was expected to bring about less fungicide based agrochemical pollution in the district since the seed spraying technique provides the lower application amount and lower tendency to spread to the environment. In this context, it was concluded that the current agricultural profile of the district is compatible with the below-EQS concentrations of the fungicides observed at the Y-1 sampling station located within the boundaries of the district.

3.4.4.1.2 Kelkit District (Y-2 Sampling Station)

Agricultural crop diversity in the Kelkit District is more extensive compared to the number of agricultural crop types raised in the Köse District. Even though a larger variety of agricultural crops are cultivated in Kelkit, the bovine husbandry activities prevail over the agricultural activities of the district. Hence, forage crops like alfalfa, sainfoin, and barley are commonly raised in this district in order to supply feed to bovine animals. In this district, these forage crops are not exposed to intensive agrochemical usage since these crops serve as feed for the animal husbandry activities performed in the district (Personal Communication with the Agricultural Engineers of Kelkit District Directorate of Agriculture and Forestry, 2019). As it is presented in Table 3.5, it was calculated that the cereal crops (wheat, barley, sainfoin and rye) and the pasture plants (alfalfa), which are colored with red in the table, are responsible for 85.2% of the total farmlands of the Kelkit District. Even though these crops cover a substantially large agricultural area in the district, their agrochemical usage schedule obtained by the agricultural engineers of Kelkit District Directorate of Agriculture and Forestry (2019) states that these crops are not protected by agrochemicals due to their usage as animal feed. In addition to these crops, maize, bean, potato and cabbage plants colored with red in Table 3.5 were also determined as the dominant crops of the Kelkit District because at least one of their district-scale and basin-scale areal percentage shares were calculated as above 5%.

Table 3.5 The Calculated Percentage Shares of the Crop Areas in the Kelkit District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Kelkit District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Wheat	62202	**40**	2.1
Barley	38852	**25**	4.9
Alfalfa	21000	**13**	**8.7**
Sainfoin	11500	**7**	**24.1**
Maize	8000	**5**	2.7
Bean	4400	3	**7.6**
Potato	3500	2	**8.0**
Sugarbeet	3070	2	1.8
Apple	990	0.6	3.5
Walnut	382	0.2	0.8
Rye	376	0.2	**8**
Triticale	312	0.2	0.2
Cabbage	250	0.2	**6.5**
Onion	144	0.1	0.1
Cucumber	105	0.1	0.6
Other Crops	Negligibly Small Portion		

3.4.4.1.2.1 Determination of the Potential Sources of Insecticide Pollution at the Y-2 Sampling Station of Kelkit

As it is given in Table 3.6, dichlorvos was determined as the only insecticide that exceed its EQS values at the Y-2 sampling station. Both of the AA-EQS and MAC-EQS values were exceeded by dichlorvos with considerably high exceedance percentages, which were calculated as 5330% and 29069%, respectively. At the Y-2 sampling station of the district, dichlorvos was observed two times out of eight sampling periods with 25% detection frequency.

When the insecticide spraying schedule of the district, which was obtained by contacting the agricultural engineers of Kelkit District Directorate of Agriculture and Forestry (2019) was assessed, it was seen that among the pre-determined dominant crops of the district, only bean and potato are sprayed by the insecticides in the Kelkit District. Except for the bean and potato crops, there are no other dominant agricultural crops that are sprayed by insecticides in the Kelkit District. For the removal of potato bugs and red bean spiders, potato and bean crops are both sprayed by insecticides in the month of August in the Kelkit District (Personal Communication with the Agricultural Engineers of Kelkit District Directorate of Agriculture and Forestry, 2019).

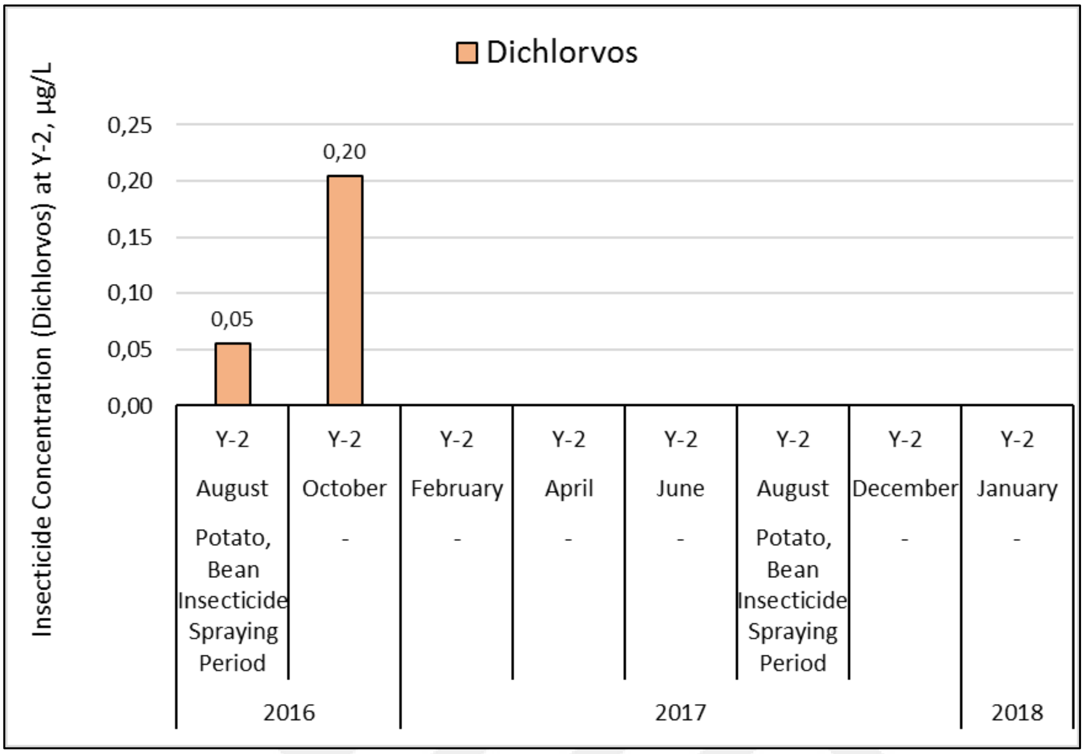

Figure 3.9 Correlation Between EQS Exceedance Months of Insecticides (at Y-2) and Insecticide Spraying Periods for the Dominant Crops of Kelkit

As it can be seen from Figure 3.9, the concentration of dichlorvos insecticide was determined as above its EQS values in the August and October sampling periods. As it was mentioned, the month of August is the insecticide spraying period of the bean and potato crops in Kelkit since these crops are attacked by the insects that occur specific to this month in the district. Regarding the temporal relation between the insecticide application months and insecticide observation months, it was revealed that the EQS exceedance of dichlorvos in the August sampling period is compatible with the insecticide spraying period of potato and bean crops raised in the district. In addition to August, October was also determined as the month of EQS exceedance for dichlorvos. Even though the month of October does not include any spraying activity of any crops in the district, the insecticide observations at the Y-2 sampling station in the October sampling period were expected since the precipitation trend of the district, which is obtained by the district-specific climate database of Meteoblue (2019), is drastically increasing in October. Transportation of dichlorvos from the applied agricultural field to the river requires driving forces like intense rainfall events, which is strongly observed in October in Kelkit. The monthly average precipitation amounts of the Kelkit District are 9 mm and 42 mm in August and October, respectively (Meteoblue Climate History in Kelkit, 2019). This sudden increase in the precipitation amount from August to October is likely to bring about increasing dichlorvos wash from the applied potato and bean fields to the river. Since there is no insecticide spraying for any dominant crop of the district in October, the insecticide spraying activities of potato and bean in August are likely to be responsible for the October detections of dichlorvos at the Y-2 sampling station based on the drastic increase in the precipitation amount of Kelkit in October. All in all, as it is shown in Figure 3.9, it was determined that there is a temporal correlation between the months of EQS exceedance of dichlorvos insecticide and the month of insecticide spraying of the bean and potato crops in Kelkit. In this respect, the bean and potato croplands, which occupy 4400 da and 3500 da areas, respectively, in the district, were determined as the potential sources of the observed dichlorvos pollution at the Y-2 sampling station of the district.

Table 3.6 Potential Sources and Detection Percentages of the Insecticides Observed at the Y-2 Sampling Station of Kelkit

Stations	**Insecticide**	**EQS Exceedance, %**		**Detection Frequency %**	**Potential Sources of the Observed Insecticides**
		AA-EQS	**MAC-EQS**		
Y-2	Dichlorvos	5330	29069	25	**Agricultural Source:** - Bean Farmland: 4400 da - Potato Farmland: 3500 da **Industrial Source:** - Wastewater Discharges of the Animal Feed Industry and the Fruit Processing Industry

Regarding contribution to the insecticide pollution of industrial sources, the wastewater discharges of the animal feed industry (Tataroğlu Flour, Animal Feed and Food Industry) and fruit processing industry (Özgümüş Food and Beverage Industry) located within the boundaries of the district were also determined as potential sources of the insecticide pollution observed at the Y-2 sampling station.

3.4.4.1.2.2 Determination of the Potential Sources of Herbicide Pollution at the Y-2 Sampling Station of Kelkit

As it is presented in Table 3.7, bifenox was determined as the only herbicide that exceeds its EQS values at the Y-2 sampling station. It was calculated that bifenox herbicide exceeded both of its MAC-EQS and AA-EQS values with 366% and 275%, respectively. The detection frequency of bifenox was determined as 25%, which implies two observations out of eight sampling periods. As it is given in Figure 3.10, these two observations belong to June and August sampling periods. When the herbicide spraying schedules of the dominant crops of the district, which is introduced by agricultural engineers of Kelkit District Directorate of Agriculture and Forestry (2019), were examined, maize was determined as the only dominant crop that has herbicide application schedule coinciding with the period of EQS exceedance of bifenox herbicide at the Y-2 sampling station.

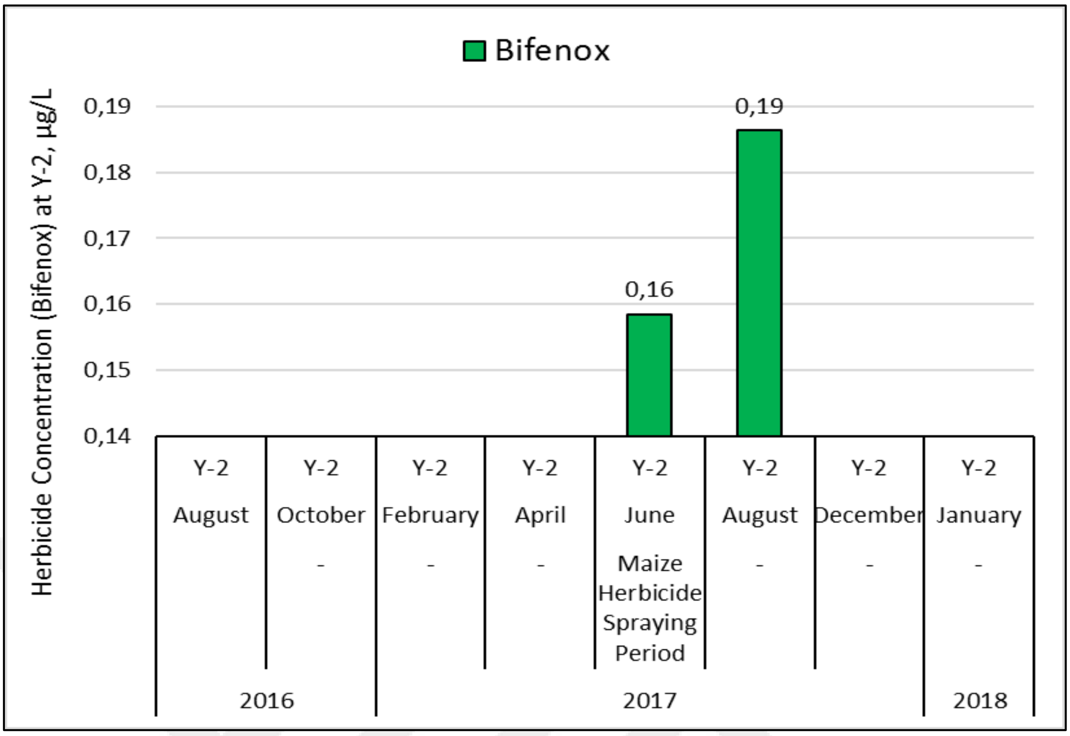

Figure 3.10 Correlation Between EQS Exceedance Months of Herbicides (at Y-2) and Herbicide Spraying Periods for the Dominant Crops of Kelkit

As it is provided in Figure 3.10, June, which is the herbicide application month of maize crop in the district, was determined as the EQS exceedance month of the bifenox herbicide. As being the following sampling period of June, August was also determined as being responsible for the high bifenox concentrations at the Y-2 sampling station. Even though in the month of August, the herbicide spraying activities are not implemented for any dominant crops of the district, the bifenox observation in this month was expected since the impact of June applications is prone to be also seen in August due to the changes in the intensity of the driving forces for the wash of herbicides like irrigation. In this respect, it was determined that the EQS exceedance periods of bifenox herbicide at the Y-2 sampling station of Kelkit are strongly correlated with the maize herbicide spraying schedule of the district. As a result of all these assessments, 8000 da maize field in Kelkit was determined as the potential source of the bifenox pollution observed at the Y-2 sampling station of the district.

Table 3.7 Potential Sources and Detection Percentages of the Herbicides Observed at the Y-2 Sampling Station of Kelkit

Stations	**Herbicide**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Herbicides**
		AA-EQS	**MAC-EQS**		
Y-2	Bifenox	275	366	25	**Agricultural Source:** - Maize Farmland: 8000 da **Industrial Source:** - Wastewater Discharges of the Animal Feed Industry and the Fruit Processing Industry

3.4.4.1.2.3 Determination of the Potential Sources of Fungicide Pollution at the Y-2 Sampling Station of Kelkit

In the Kelkit District, fungicide pollution was not observed at the Y-2 sampling station.

3.4.4.2 Giresun Province

The Giresun Province embodies Y-3 and Y-4 sampling stations, which are located within the boundaries of the Çamoluk District and the Şebinkarahisar District, respectively. Since the Çamoluk District and the Şebinkarahisar District have considerably high altitude as 1372 m and 1062 m, respectively, and they are both located in the interior of the Giresun Province, the agricultural activities in these two districts are not intensive compared to the other districts of the province that are under the effect of sea climate. In these districts, agricultural activities are typically performed in order to serve animal feed sectors (Personal Communication with the Agricultural Engineers of Giresun Provincial Directorate of Agriculture and Forestry, 2019). The typical agricultural profiles of the Çamoluk and Şebinkarahisar districts are discussed in Section 3.4.4.2.1 and Section 3.4.4.2.2, respectively. Besides, with the analysis of pesticide concentration data of the Y-3 and Y-4 sampling stations, the degree and type of the pesticide pollution observed at these sampling stations and the potential sources of the observed pesticide pollution within the boundaries of the Çamoluk and Şebinkarahisar districts are assessed within the scope of the above-mentioned sections in detail.

3.4.4.2.1 Çamoluk District (Y-3 Sampling Station)

Among all 26 districts of the basin, the Çamoluk District has the smallest agricultural land with 10546 da total agricultural area. In this district, agricultural activities are limited since topography of the district is typically rough and formed by high altitude features, which provide a favorable environment for the dominance of animal husbandry activities rather than agriculture (Personal Communication with the Agricultural Engineers of Çamoluk District Directorate of Agriculture and Forestry, 2019). The diversity of agricultural products raised in the Çamoluk District is limited to the animal feed crops like wheat, sainfoin and alfalfa, which all occupy small cultivation areas in the district. Consequently, agrochemical usage is not a common agricultural practice in the farmlands of the district. According to the agricultural engineers of Çamoluk District Directorate of Agriculture and Forestry (2019), the agricultural lands of Çamoluk are not sprayed by pesticides since the agricultural activities implemented in this district are limited to small farmlands and not performed for the purpose of commercial profit. In this context, it was concluded that there is no justifiable relation between the agricultural land use and the pesticide pollution observed at the Y-3 sampling station of Çamoluk. Hence, it was determined that the agricultural fields of Çamoluk do not have the potential to be the source of the observed pesticide pollution. On the other hand, as it is presented in Table 3.8, the concentrations of dichlorvos, fenpropathrin and aclonifen pesticides were determined as above their EQS values at the Y-3 sampling station of Çamoluk, which indicates that, unlike agricultural activities, there exist other pesticide pollution sources that are responsible for these observations.

Table 3.8 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-3 Sampling Station of Çamoluk

Stations	**Pesticides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Pesticides**
		AA-EQS	**MAC-EQS**		
Y-3	Dichlorvos	1362	9676	12.5	**Agricultural Source:** - Not Exist **Industrial Source:** - Not Exist
	Fenpropathrin	21	515	12.5	
	Aclonifen	-	375	12.5	

As it is provided in Table 3.8, it was calculated that all of the three pesticides were exceeded their EQS values only in one sampling period out of eight observations corresponding to 12.5% detection frequency. Due to the nonpersistent and immobile characteristics of the observed pesticides in the basin, which were discussed in Section 3.4.2.2 and Section 3.4.2.3, the potential sources of the pesticides were investigated only within the boundaries of the district and its surrounding environment rather than the remote districts. In this respect, when the industrial activities performed within the boundaries of Çamoluk were examined, it was revealed that there is no pesticide usage related industry exist in this district. All in all, the observed pesticide pollution was not attributed to the agricultural and industrial activities performed in the Çamoluk District. Wastewater discharges from UWWTPs of the district, pesticide releases from animal husbandry activities and pesticide transport from the surrounding districts can be listed as possible sources of the observed pesticide pollution.

3.4.4.2.2 Şebinkarahisar District (Y-4 Sampling Station)

In the Şebinkarahisar District, the agricultural products obtained from the agricultural fields of the district typically serve the animal husbandry activities as animal feed. In parallel with the highly intensive animal husbandry activities of the district, the agricultural activities are mainly based on grain cultivation like wheat and barley crops. Compared to the Çamoluk District, the Şebinkarahisar District embodies relatively larger agricultural lands; however, the agricultural products raised in this district are low in diversity. In other words, the agricultural products raised in the district are predominantly composed of grain-type crops with high cultivation areas. As it is given in Table 3.9, wheat and barley were identified as the dominant crops of the Şebinkarahisar District with 55% and 37% areal shares among the other crops of the district, respectively. The total area of the wheat and barley crops were determined as being accountable for 92% of total agricultural lands in Şebinkarahisar. The calculated percentage shares of the wheat and barley areas show that almost the entire agricultural lands of the district are occupied by wheat and barley fields.

Table 3.9 The Calculated Percentage Shares of the Crop Areas in the Şebinkarahisar District

Agricultural Crop	Area of Agricultural Land, decare (TurkStat, 2020)	Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Şebinkarahisar District, %	Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %
Wheat	83612	**55**	2.8
Barley	57500	**37**	**7.3**
Alfalfa	5040	3	2.1
Sainfoin	2100	1	4.4
Triticale	1234	1	0.9
Walnut	1050	1	2.3

Table 3.9 (cont'd)

Agricultural Crop	Area of Agricultural Land, decare (TurkStat, 2020)	Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Şebinkarahisar District, %	Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %
Sweet Cherry	760	0.5	2.0
Apple	715	0.5	2.6
Potato	690	0.4	1.6
Bean	113	0.1	0.2
Other Crops	Negligibly Small		

3.4.4.2.2.1 Determination of the Potential Sources of Insecticide Pollution at the Y-4 Sampling Station of Şebinkarahisar

As it is provided in Table 3.10, the concentration of three different insecticides, which are dichlorvos, diflubenzuron and HCH, were calculated as above their EQS values at the Y-4 sampling station of the Şebinkarahisar District. It was determined that among these insecticides, dichlorvos exceeded both of its AA-EQS and MAC-EQS values with 2293% and 16057%, respectively. On the other hand, diflubenzuron and HCH insecticides exceeded only their MAC-EQS values with relatively lower exceedance percentages compared to dichlorvos. Regarding the calculated detection frequencies of the insecticides, it was determined that HCH exceeded its EQS value in two measurements out of eight sampling periods, dichlorvos and diflubenzuron exceeded their EQS values only in one measurement out of eight sampling periods.

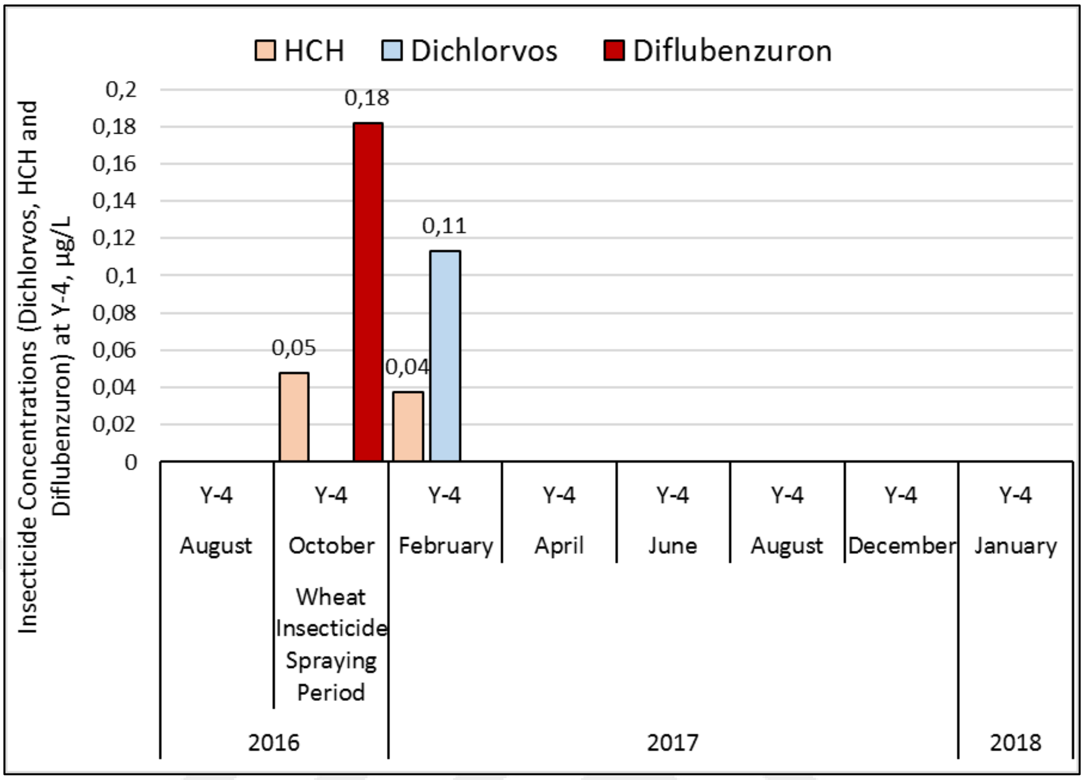

Figure 3.11 Correlation Between EQS Exceedance Months of Insecticides (at Y-4) and Insecticide Spraying Periods for the Dominant Crops of Şebinkarahisar

As it was explained, wheat and barley were determined as the dominant crops of the Şebinkarahisar District based on their remarkably high areal percentages. When the insecticide spraying schedules of wheat and barley, which were obtained by contacting with the agricultural engineers of the Şebinkarahisar District Directorate of Agriculture and Forestry (2019), were examined, it was revealed that while the wheat crop is sprayed by the insecticides in October, the barley crop does not have any insecticide application in the Şebinkarahisar District. As it is shown in Figure 3.11, it was determined that the concentrations of diflubenzuron and HCH were observed as above their EQS values in the month of October. Based on the temporal relation between the insecticide spraying month of the wheat crop and the EQS exceedance month of the diflubenzuron and HCH insecticides, the 83612 da wheat cropland, which corresponds to 55% of the total agricultural land use of Şebinkarahisar, was determined as the potential source of the diflubenzuron and HCH pollution observed at the Y-4 sampling station of Şebinkarahisar.

Table 3.10 Potential Sources and Detection Percentages of the Insecticides Observed at the Y-4 Sampling Station of Şebinkarahisar

Stations	**Insecticide**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Insecticides**
		AA-EQS	**MAC-EQS**		
Y-4	Diflubenzuron	-	40	12.5	**Agricultural Source:** - Wheat Farmland: 83612 da **Industrial Source:** - Wastewater Discharges of the Animal Feed Production Industry
	HCH	-	19	25	
	Dichlorvos	2293	16057	12.5	**Agricultural Source:** - Not Exist **Industrial Source:** - Wastewater Discharges of the Animal Feed Production Industry

As it was stated by the agricultural engineers of the Şebinkarahisar District Directorate of Agriculture and Forestry (2019), in the month of February, the agricultural crops are not protected by the insecticides due to the absence of insect infestations under the cold winter conditions in Şebinkarahisar. Even though the agrochemicals are not used in the farmlands of Şebinkarahisar in February, the dichlorvos and diflubenzuron insecticides were observed in the February sampling period. Since the agricultural spraying practices are not performed in the January-February season due to the harsh climatic conditions in the district (Personal Communication with the Agricultural Engineers of Şebinkarahisar District Directorate of Agriculture and Forestry, 2019), diflubenzuron and dichlorvos pollution observed in February can be related to the wastewater discharges from the industrial activities that use pesticides or use raw materials exposed to pesticides in their processes. When the industries located within the boundaries of Şebinkarahisar were investigated, it was revealed that the animal feed facility (Has Hisar Animal Feed Production Industry) is the only industry that integrates pesticide usage in its processes and discharges its wastewater to the river. In this respect, the wastewater discharge from the animal feed industry was also determined as having the potential to contribute to the insecticide pollution observed at theY-4 sampling station of the Şebinkarahisar District.

3.4.4.2.2.2 Determination of the Potential Sources of Herbicide Pollution at the Y-4 Sampling Station of Şebinkarahisar

As it is given in Table 3.11, aclonifen was determined as the only herbicide that exceeded its EQS value at the Y-4 sampling station of Şebinkarahisar. It was calculated that aclonifen exceeded only its MAC-EQS value as 282% in one measurement out of eight sampling periods, which corresponds to 12.5% detection frequency.

As it was reported by the agricultural engineers of Şebinkarahisar District Directorate of Agriculture and Forestry (2019), herbicides are not used on the farmlands of the Şebinkarahisar District. Since there is no herbicide spraying activity performed in the district, the observed herbicide pollution was not attributed to the agricultural land use. Regarding the impact of industrial activities, the wastewater discharge from the animal feed industry (Has Hisar Animal Feed Production Industry), which was mentioned in Section 3.4.4.2.2.1, was determined as having the potential to be responsible for the observation of the aclonifen herbicide at the Y-4 sampling station of the Şebinkarahisar District.

Table 3.11 Potential Sources and Detection Percentages of the Herbicides Observed at the Y-4 Sampling Station of Şebinkarahisar

Stations	Herbicide	EQS Exceedance %		Detection Frequency %	Potential Sources of the Observed Herbicides
		AA-EQS	MAC-EQS		
Y-4	Aclonifen	-	282	12.5	**Agricultural Source:** - Not Exist **Industrial Source:** - Wastewater Discharges of the Animal Feed Production Industry

3.4.4.2.2.3 Determination of the Potential Sources of Fungicide Pollution at the Y-4 Sampling Station of Şebinkarahisar

In the Şebinkarahisar District, fungicide pollution was not observed at the Y-4 sampling station. The absence of fungicide-based pesticide pollution in the boundaries of Şebinkarahisar was expected because when the pesticide application schedule of the district is taken into account, it was revealed that the fungicides are not used in the farmlands of Şebinkarahisar due to the cold and dry climate, which prevent the occurrence of fungal diseases on the agricultural crops raised in this district (Personal Communication with the Agricultural Engineers of Şebinkarahisar District Directorate of Agriculture and Forestry, 2019).

3.4.4.3 Sivas Province

Different from the provinces in the western part of the basin, the intensity of the agriculture in the eastern provinces like Sivas, Giresun and Gümüşhane is suppressed by the eastern climate and topography. Therefore, like in the case of the Giresun and Gümüşhane provinces, the agricultural profile of the Sivas Province is also under the effect of animal husbandry activities, which typically prevail in the eastern regions of the basin. The Sivas Province embodies Y-5 and Y-6 water quality measurement stations, which are located in the Koyulhisar and Zara districts of the province, respectively. The potential sources of the pesticide pollution observed at the Y-5 and Y-6 sampling stations of the Koyulhisar and Zara districts were determined and discussed in Section 3.4.4.3.1 and Section 3.4.4.3.2, respectively. Furthermore, within the scope of the above-mentioned sections, the localized agricultural management trends of these two districts were investigated and their relation with the observed pesticide pollution was assessed by analyzing the degree and type of the pesticide pollution at the corresponding sampling stations of each of the districts.

3.4.4.3.1 Koyulhisar District (Y-5 Sampling Station)

Agricultural activities in the Koyulhisar District are not intense in parallel with the small crop cultivation area and low crop diversity of the farmlands of the district. After the Çamoluk District, Koyulhisar is the second district that has the lowest total agricultural area among the 26 districts of the basin. With 24996 da total agricultural land occupation, the Koyulhisar District has a considerably low areal share for agricultural activities. This limited agricultural land use in the Koyulhisar District is typically based on forage crop cultivation, which involves the farming of grain crops like wheat and barley and pasture crops like alfalfa. The forage crops typically do not require intense agrochemical usage since the required level of food security for the grain-type crops that are raised to serve the livestock activities is relatively low compared to the grain-type crops raised to serve to food sectors. In the Koyulhisar District, the grain and pasture crops like wheat, alfalfa, barley and sainfoin are raised for the purpose of usage as animal feed; thus, plant protection by agrochemicals is not implemented as a part of the agricultural activities in this district. (Personal Communication with the Agricultural Engineers of Koyulhisar District Directorate of Agriculture and Forestry, 2019). As it is provided in Table 3.12, it was calculated that the total area of the forage plants (wheat, alfalfa, sainfoin and barley) occupy 90% of the total agricultural land in Koyulhisar. However, the areal shares of these crops among the areas of the same crop types raised in the 26 districts of the basin were calculated as notably low. For instance, when the areal percentage shares given in Table 3.12 are examined, it can be seen that the percentage share of the wheat area in Koyulhisar among the wheat areas raised in the other districts of the basin was determined as 0.3%, which is substantially low percentage regarding the possible contribution of these croplands to the agrochemical usage in the entire basin. All in all, since the dominant agricultural crops of the district were determined as being primarily composed of the grains with low areal percentage shares in the basin and these grains serve to the animal feed facilities rather than the commercial food sectors, the agrochemical usage is not common agricultural practice in Koyulhisar. Therefore, it was concluded that the agricultural lands of Koyulhisar are not expected to be the possible source of the pesticide pollution in the basin.

Table 3.12 The Calculated Percentage Shares of the Crop Areas in the Koyulhisar District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Koyulhisar District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Wheat	9536	**38**	0.3
Alfalfa	6700	**27**	2.8
Sainfoin	3800	**15**	**8.0**
Barley	2562	**10**	0.3
Walnut	1231	**5**	2.7
Bean	335	1	0.6
Tomato	205	1	0.3
Apple	119	0.5	0.4
Other Crops	Negligibly Small Portion		

As it is given in Table 3.13, dichlorvos, bifenox and ethalfluralin were determined as the pesticides that exceeded their EQS values at the Y-5 sampling station of the Koyulhisar District. Among these three pesticides, it was calculated that only dichlorvos exceeded both of its AA-EQS and MAC-EQS values with 4455% and 23426%, respectively. On the other hand, bifenox and ethalfluralin exceeded only their MAC-EQS values with 70% and 170%, respectively. Compared to the dichlorvos insecticide, bifenox and ethalfluralin herbicides are posing relatively less concern to the river pollution on an annual basis since the concentrations of bifenox and ethalfluralin were determined as below their AA-EQS values. Regarding fungicide-based pesticide pollution, it was determined that there is no fungicide detection that exceeded the EQS values at the Y-5 sampling station. All in all, the observed dichlorvos, bifenox and ethalfluralin detections at the Y-5 sampling station point out that there exist pesticide pollution sources that have potential to be accountable for these observations.

As it was explained, due to the general agricultural profile of Koyulhisar, which is typically based on the cultivation of animal feed grains with low areal shares at the basin scale, the pesticide detections were not associated with the agricultural land use of Koyulhisar. Even though the forage crops raised for the purpose of usage as animal feed are not sprayed by agrochemicals during agricultural production, they can be exposed to high pesticide usage during the storage and processing steps of animal feed production facilities. In this respect, when the pesticide usage related industrial facilities were examined within the boundaries of Koyulhisar, it was revealed that the Koyulhisar District embodies animal feed production industry (Fırat Flour, Agriculture, Livestock and Food Material Production Facility), which discharges its wastewater into the river basin within the boundaries of this district. Therefore, it was concluded that the wastewater discharges of this industrial facility has the potential to be responsible for the EQS exceedances of the dichlorvos, bifenox and ethalfluralin pesticides, which were occasionally observed at the Y-5 sampling station of the Koyulhisar District.

Table 3.13 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-5 Sampling Station of Koyulhisar

Stations	**Pesticides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Pesticides**
		AA-EQS	**MAC-EQS**		
Y-5	Dichlorvos	4455	23426	25	**Agricultural Source:** - Not Exist **Industrial Source:** - Wastewater Discharges of the Animal Feed Production Industry
	Bifenox	-	70	12.5	
	Ethalfluralin	-	170	12.5	

3.4.4.3.2 Zara District (Y-6 Sampling Station)

In the Zara District, the abundance of mountainous areas favors animal husbandry activities in the district. The Zara District has a 1344 m elevation, which is a relatively high altitude compared to other districts of the basin. In parallel with the high altitude topography, animal husbandry activities intensively prevail in the district; consequently, the agricultural land use in this district is almost entirely based on the forage cultivation, which comprises the grain fields and pastures (Personal Communication with the Agricultural Engineers of Zara District Directorate of Agriculture and Forestry, 2019). As it is presented in Table 3.14, it was calculated that the forage plants (wheat, alfalfa, sainfoin, oat, triticale and barley) cover 99% of the total agricultural area in Zara. The calculated high areal percentages of the forage crops prove the predominance of the animal husbandry activities in the district. Wheat, alfalfa, sainfoin and oat, which are colored with red in Table 3.14, were determined as the dominant crops of the district with their areal shares above 5%. Among these crops, alfalfa was determined as having a considerably high areal share at the basin scale. It was calculated that 18.6% of the total alfalfa cultivation of the basin is performed in the Zara District. As being one of the forage-type crops, sainfoin also has high areal contribution to the land use at the basin scale rather than the district scale. Even though the sainfoin crop was determined as having a low areal share among the other crop types raised in the district, it has a notably high areal share among the sainfoin farmlands of 26 districts of the basin. Due to the high areal occupation of sainfoin at the basin scale despite the low areal share in the other crops of Zara, sainfoin was determined as one of the dominant crops of the Zara District. The wheat crop was also identified as the dominant crop of the district since it has a high areal share (65%) among the other crop types raised in the district despite its low share (4.5%) among the wheat areas of the other districts in the basin.

Table 3.14 The Calculated Percentage Shares of the Crop Areas in the Zara District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Zara District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Wheat	132887	**65**	4.5
Alfalfa	45000	**22**	**18.6**
Sainfoin	7500	4	**15.7**
Oat	7500	4	**5.2**
Triticale	5701	3	4.3
Barley	1917	1	0.2
Sugarbeet	1484	1	0.9
Chickpea	750	0.4	0.5
Maize	450	0.2	0.2
Potato	300	0.1	0.7
Other Crops	Negligibly Small Portion		

3.4.4.3.2.1 Determination of the Potential Sources of Insecticide Pollution at the Y-6 Sampling Station of Zara

As it is given in Table 3.15 , four different types of insecticides, which are dichlorvos, diflubenzuron, fenthion and HCH, were determined as exceeding their EQS values at the Y-6 sampling station of Zara. Among these insecticides, it was calculated that only dichlorvos exceeded both of its MAC-EQS and AA-EQS values as 2321% and 10133%, respectively. While the concentrations of diflubenzuron and HCH were calculated as above only their MAC-EQS values with 65% and 22%, respectively, the concentration of fenthion was calculated as above only its AA-EQS value with 20%. All of these four insecticides were observed only in one measurement out of five sampling periods, which corresponds to 20% detection frequency.

According to the agricultural engineers of Zara District Directorate of Agriculture and Forestry (2019), the insect infestations are not intense in the agricultural lands of the district. Even though the insecticide usage in the district is not intensive, the diversity of the insecticides used in the farmlands was expected to be high due to the large areal occupation of the forage-type crops like wheat in the district. As it was explained, the wheat croplands were determined to cover substantially large area by being responsible for 18.6% of the wheat farmlands of the basin. When the insecticide application schedule of the Zara District was examined, among the dominant crops of the district, wheat is the only crop that is sprayed by insecticides. As it was stated by the agricultural engineers of Zara District Directorate of Agriculture and Forestry (2019), the seeds of the wheat crop is sprayed by insecticides in the month of October before cultivation. As it was demonstrated in Figure 3.12, the concentrations of HCH, fenthion and diflubenzuron were all determined as above their EQS values in the month of October at the Y-6 sampling station of the district. In this respect, it was revealed that there is a compatibility between the EQS exceedance periods of the HCH, diflubenzuron and fenthion insecticides observed at the Y-6 sampling station and the insecticide spraying schedule of the wheat crop in the district. As a result, the wheat crop, which was calculated as being responsible for 65% of agricultural land use of the district, was determined as the potential source of the HCH, diflubenzuron and fenthion pollution observed at the Y-6 sampling station of the Zara District.

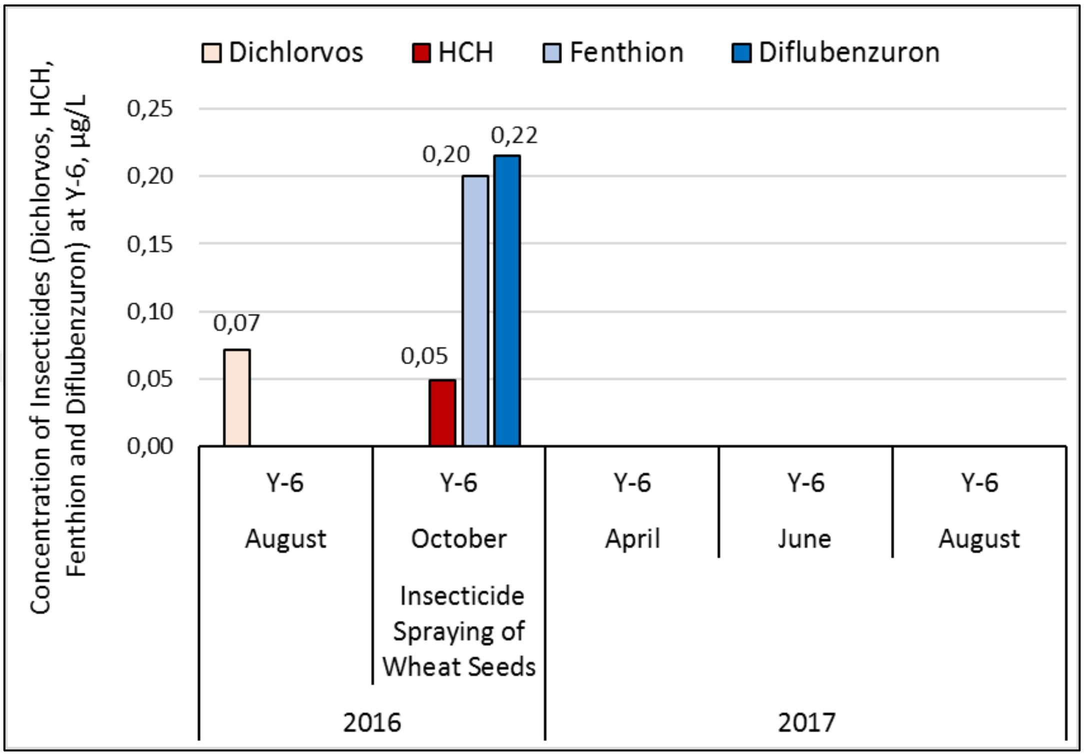

Figure 3.12 Correlation Between EQS Exceedance Months of Insecticides (at Y-6) and Insecticide Spraying Periods for the Dominant Crops of Zara

The month of October was determined as being responsible for all insecticide detections, except dichlorvos. For dichlorvos, there is an exceptional situation because, as it was explained in Section 3.4.2.3, it was determined that among all 16 pesticides observed in the entire basin, dichlorvos is the only pesticide that has the mobile characteristic, whereas all the remaining 15 pesticides are strongly immobile in the environment. Thus, the agricultural activities performed in the remote areas of the basin were also taken into account as being a potential source of the observed dichlorvos pollution due to the possible contribution of these sources to the observed pollution via transportation of dichlorvos over long distances. In this regard, despite the absence of insecticide spraying activities in the month of August in Zara, the dichlorvos observation at the Y-6 sampling station in August was expected due to the remarkably high mobility of dichlorvos, unlike the rest of the observed insecticides.

Table 3.15 Potential Sources and Detection Percentages of the Insecticides Observed at the Y-6 Sampling Station of Zara

Stations	Insecticides	EQS Exceedance %		Detection Frequency %	Potential Sources of the Observed Insecticides
		AA-EQS	MAC-EQS		
Y-6	Diflubenzuron	-	65	20	**Agricultural Source:** - Wheat Farmland: 132887 da **Industrial Source:** - Not Exist
	HCH	-	22	20	
	Fenthion	20	-	20	
	Dichlorvos	2321	10133	20	**Agricultural Sources:** - Not Exist **Industrial Sources:** - Not Exist

3.4.4.3.2.2 Determination of the Potential Sources of Herbicide Pollution at the Y-6 Sampling Station of Zara

As it is given in Table 3.16, ethalfluralin was determined as the only herbicide that was observed at the Y-6 sampling station of the Zara District. It was calculated that ethalfluralin exceeded only its MAC-EQS value with 18% exceedance and 20% detection frequency, which corresponds to one measurement out of five sampling periods. As it is demonstrated in Figure 3.13, the EQS exceedance of ethalfluralin herbicide at the Y-6 sampling station was observed only in April, which was introduced as the main herbicide spraying period for the wheat crops raised in Zara by the agricultural engineers of Zara District Directorate of Agriculture and Forestry (2019). Among the pre-determined dominant crops of the district, as it is stated in Table 3.14, the largest agricultural land of Zara belongs to the wheat crop, which was determined as being responsible for 65% of the total agricultural land in Zara. According to the herbicide application schedules of the crops raised in the Zara District, which were provided by the agricultural engineers of Zara District Directorate of Agriculture and Forestry (2019), except the wheat crop, the rest of the dominant crops of the district (alfalfa, sainfoin and oat) do not require any type of agrochemical usage including herbicides. Since almost all of the herbicide spraying activities in Zara are implemented only to the wheat crop in the month of April, the EQS exceedance of ethalfluralin herbicide, which was observed in April, was attributed to the herbicide spraying activities of the wheat fields in the Zara District. According to the monthly average precipitation data of Zara, which is obtained by the district-specific historical climate database of Meteoblue (2019), the precipitation regime in Zara reaches its maximum level in April with a 96 mm average precipitation amount. The fact that the highest monthly precipitation amount in Zara belongs to April can be seen as another factor that influences the high ethalfluralin observations in the month of April. In this regard, it was deduced that the wash and transport of the sprayed herbicides are prone to occur right after their use on the farmlands due to the high severity of the precipitation event in April, which is the month of herbicide application for the wheat crop in Zara. In the light of all these evaluations and analyzes, 132887 da wheat farmland, which was identified as one of the dominant crops of Zara with 65% occupation of the total agricultural lands in the district, was determined as the potential source of the ethalfluralin pollution observed at the Y-6 sampling station.

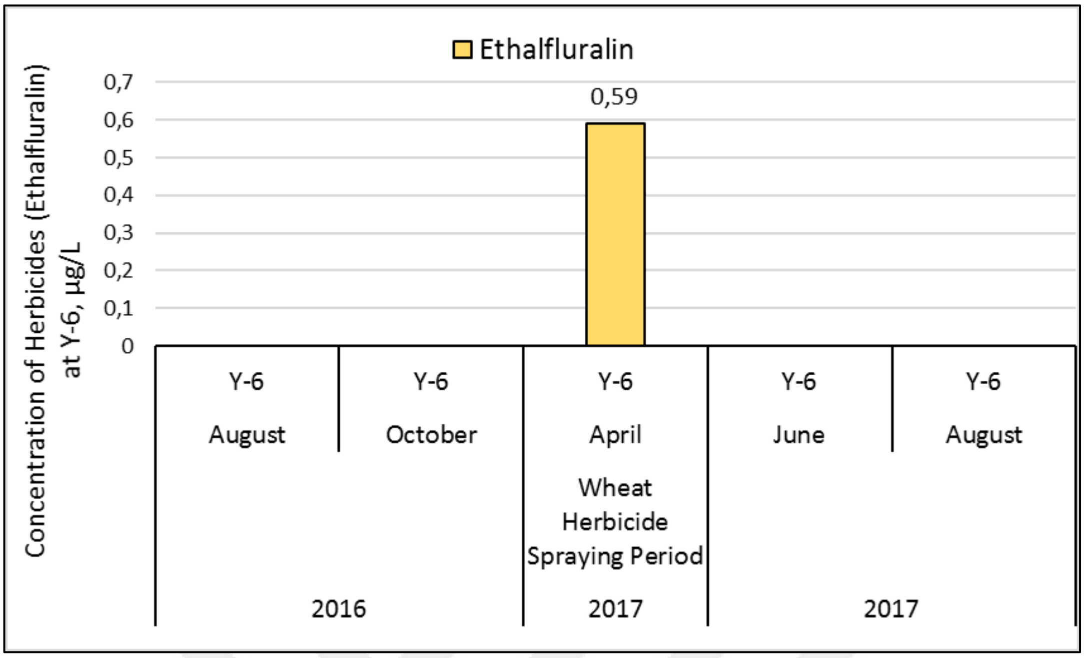

Figure 3.13 Correlation Between EQS Exceedance Months of Herbicides (at Y-6) and Herbicide Spraying Periods for the Dominant Crops of Zara

Table 3.16 Potential Sources and Detection Percentages of the Herbicides Observed at the Y-6 Sampling Station of Zara

Stations	**Herbicides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Herbicides**
		AA-EQS	**MAC-EQS**		
Y-6	Ethalfluralin	-	18	20	**Agricultural Source:** - Wheat Farmland: 132887 da **Industrial Source:** - Not Exist

3.4.4.3.2.3 Determination of the Potential Sources of Fungicide Pollution at the Y-6 Sampling Station of Zara

The fungicide-type pesticide pollution was not observed at the Y-6 sampling station of the Zara District.

So far, the pesticide usage profile of the Köse, Kelkit, Şebinkarahisar, Çamoluk, Koyulhisar and Zara districts of the Gümüşhane, Giresun and Sivas provinces, which are all located in the eastern part of the basin, were discussed, in detail. Within the scope of these assessments, the degree and type of pesticide pollution at the Y-1, Y-2, Y-3, Y-4, Y-5 and Y-6 sampling stations in these eastern districts were analyzed in order to identify the potential sources of the pesticide pollution observations. In common, in all these eastern districts, the fungicide-type pesticide pollution was not observed at any of the sampling stations. The common trait of these districts is their relatively cold and dry climate and also high topography compared to the western districts of the basin. The impact of the relatively cold climate and high altitude of these eastern districts can be one of the potential reasons for the below-EQS observations for the fungicides. The studies conducted by Rhodes & McCarl (2020), Coakley et al. (1999) and Braisier (1996) emphasize that the intensity of fungal diseases in the farmlands of the regions that have high temperature and humidity is less compared to the territories under the low humidity and low temperature conditions. In this respect, the assessment results for the the Köse, Kelkit, Şebinkarahisar, Çamoluk, Koyulhisar and Zara districts, which were discussed so far comprehensively, showed that the absence of fungicide pollution observed at the corresponding sampling stations is a common outcome of the typical geographic and climatic characteristics of these eastern districts of the basin. The degree and type of pesticide pollution in the western part of the basin, and its potential sources will be identified and discussed in the following sections.

3.4.4.4 Tokat Province

The Tokat Province has the second largest agricultural lands in the basin after the Amasya Province. The water quality measurement stations are located in the eight districts of Tokat, which are composed of Reşadiye, Niksar, Merkez, Almus, Pazar, Sulusaray, Turhal and Erbaa districts. As it is stated by the agricultural engineers of Tokat Provincial Directorate of Agriculture and Forestry (2019), the agricultural profiles of these eight districts of Tokat can be distinctively different from each other since the climate of Tokat incorporates various microclimates, which brings about variability in the intensity and type of the pest attacks that occur in the same crop types raised in the different districts of Tokat. In this context, the analysis of the degree and type of the pesticide pollution at the corresponding sampling stations and the identification of pesticide pollution sources were performed with individual assessments by taking into account the variability in the agricultural profiles and the pest management practices for each of the eight districts of Tokat.

3.4.4.4.1 Reşadiye District (Y-7, Y-8, Y-9 Sampling Stations)

In the Reşadiye District, the major part of land use consists of forestlands and semi-natural areas, which are responsible for %67 of total land use of the district. Regarding the geographical characteristic of Reşadiye, the district has a 534 m elevation, which brings about large planes covered by pasture areas used for the ovine-type animal husbandry. The agricultural land use of the district has evolved in parallel with animal husbandry activities. The agriculture of the district is substantially based on pastures and cereal fields, which arise from the need for sheep and goat breeding activities in Reşadiye (Personal Communication with the Agricultural Engineers of Reşadiye District Directorate of Agriculture and Forestry, 2019). As it is given in Table 3.17, it was determined that the forage plant cultivation, which is composed of wheat, barley, triticale, sainfoin and alfalfa crops, is responsible for 91% of the total agricultural land use in Reşadiye. Different from the forage type crops, walnut, cherry and cabbage plants were also determined as the dominant crops of Reşadiye by occupying a significantly large areas among the walnut, cherry and cabbage areas cultivated in the other districts of the basin. The basin-wide areal shares of the walnut, cherry and cabbage crops of Reşadiye were calculated as 8%, 8.2% and 10%, respectively.

Table 3.17 The Calculated Percentage Shares of the Crop Areas in the Reşadiye District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Reşadiye District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Wheat	63554	**66**	2.1
Barley	9296	**10**	1.2
Triticale	8636	**9**	**6.5**
Sainfoin	4225	4	**8.9**
Walnut	3664	4	**8.0**
Alfalfa	2095	2	0.9
Potato	1241	1	2.8
Bean	1040	1	1.8
Chickpea	1000	1	0.9
Cherry	445	0.5	**8.2**
Cabbage	380	0.4	**10.0**
Maize	267	0.3	0.1
Apple	261	0.3	0.9
Pear	130	0.1	2.7
Tomato	130	0.1	0.2
Other Crops	Negligibly Small Portion		

3.4.4.4.1.1 Determination of the Potential Sources of Insecticide Pollution at the Y-7, Y-8 and Y-9 Sampling Stations of Reşadiye

As it is presented in Table 3.18, regarding insecticide group, dichlorvos and fenthion were observed at the Y-7, Y-8 and Y-9 sampling stations of Reşadiye. Dichlorvos insecticide was determined as exceeding both of its AA-EQS and MAC-EQS values at all three sampling stations of Reşadiye with 37.5%, 25% and 12.5% detection frequencies; whereas, fenthion insecticide was determined as exceeding only its MAC-EQS value only at the Y-8 sampling station with 12.5% detection frequency. When it is compared to dichlorvos, fenthion has a notably low EQS exceedance level with low detection frequency. All in all, among these two insecticides, dichlorvos was determined as the major insecticide type of Reşadiye regarding its high contribution level to the insecticide pollution and high observation frequencies at all three sampling stations of Reşadiye.

Table 3.18 Potential Sources and Detection Percentages of the Insecticides Observed at the Y-7, Y-8 and Y-9 Sampling Stations of Reşadiye

<table>
<tr><th rowspan="2">Stations</th><th rowspan="2">Insecticides</th><th colspan="2">EQS Exceedance %</th><th rowspan="2">Detection Frequency %</th><th rowspan="2">Potential Sources of the Observed Insecticides</th></tr>
<tr><th>AA-EQS</th><th>MAC -EQS</th></tr>
<tr><td>Y-7</td><td>Dichlorvos</td><td>4589</td><td>15212</td><td>37.5</td><td rowspan="4">Agricultural Source:
- Cherry Farmland: 445 da
- Cabbage Farmland: 380 da
Industrial Source:
- Not Exist</td></tr>
<tr><td rowspan="2">Y-8</td><td>Dichlorvos</td><td>5469</td><td>20297</td><td>25</td></tr>
<tr><td>Fenthion</td><td>46</td><td>-</td><td>12.5</td></tr>
<tr><td>Y-9</td><td>Dichlorvos</td><td>8222</td><td>42023</td><td>29</td></tr>
</table>

When the industrial facilities that discharge their wastewater to the river within the boundaries of Reşadiye were examined, it was revealed that the Reşadiye District does not embody the industrial facilities that use the pesticides in their processes or raw materials exposed to the pesticides. The absence of these industries within the boundaries of Reşadiye points out the agricultural activities as being the potential source of the insecticide pollution observed at the sampling stations of the district. In this respect, the localized agricultural practices of Reşadiye were assessed in order to identify the agricultural sources that have the potential to contribute to insecticide pollution. As it is stated by the agricultural engineers of Reşadiye District Directorate of Agriculture and Forestry (2019), the insecticide usage in the district is mainly performed on fruits and vegetables rather than forage crops like barley and alfalfa. As it is shown in Figure 3.14, the concentrations of dichlorvos and fenthion insecticides at the sampling stations of Reşadiye were calculated as above their EQS values, primarily in the months of August and October. When the insecticide spraying schedules of the dominant crops of Reşadiye were examined, it was revealed that the month of August is responsible for the insecticide spraying of the cabbage croplands in Reşadiye. In the month of October, the protection of cherry crops against insect attacks is carried out via insecticide spraying in the district (Personal Communication with the Agricultural Engineers of Reşadiye District Directorate of Agriculture and Forestry, 2019). Among the pre-determined dominant crops of Reşadiye, only the cabbage and cherry crops have insecticide spraying schedule in the months of August and October, which are responsible for the intense dichlorvos and fenthion observations in Reşadiye; hence, the existence of these insecticides was attributed to the cabbage and cherry lands of the district. All in all, it was concluded that since the insecticide spraying months of the cherry and cabbage crops in Reşadiye strongly coincide with the months of EQS exceedance of the dichlorvos and fenthion insecticides, the cherry and cabbage croplands of the district were identified as the potential sources of the dichlorvos and fenthion pollution observed at the sampling stations of Reşadiye.

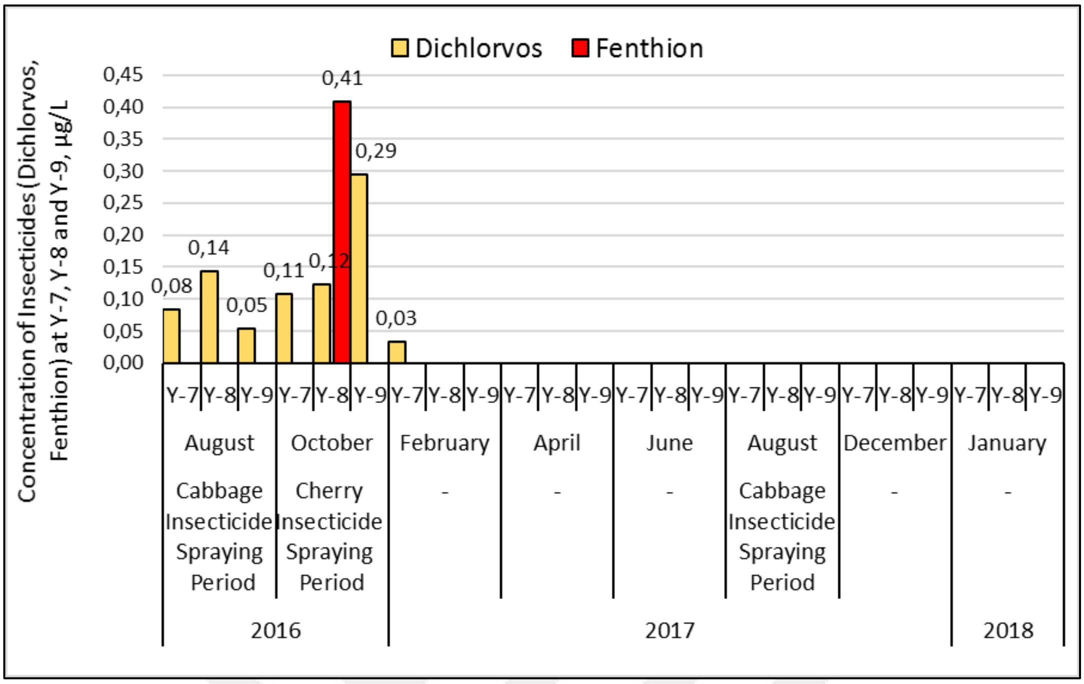

Figure 3.14 Correlation Between EQS Exceedance Months of Insecticides (at Y-7, Y-8 and Y-9) and Insecticide Spraying Periods for the Dominant Crops of Reşadiye

3.4.4.4.1.2 Determination of the Potential Sources of Herbicide Pollution at the Y-7, Y-8 and Y-9 Sampling Stations of Reşadiye

The herbicide-type pesticide pollution was not observed at any of the Y-7, Y-8 and Y-9 sampling stations of Reşadiye.

3.4.4.4.1.3 Determination of the Potential Sources of Fungicide Pollution at the Y-7, Y-8 and Y-9 Sampling Stations of Reşadiye

As it is provided in Table 3.19, fenpropimorph was determined as the only fungicide type that was observed at the sampling stations of Reşadiye by exceeding only its AA-EQS with 76% in one observation out of eight sampling periods.

Table 3.19 Potential Sources and Detection Percentages of the Fungicides Observed at the Y-7, Y-8 and Y-9 Sampling Stations of Reşadiye

<table>
<tr><th rowspan="2">Stations</th><th rowspan="2">Fungicides</th><th colspan="2">EQS Exceedance %</th><th rowspan="2">Detection Frequency %</th><th rowspan="2">Potential Sources of the Observed Fungicides</th></tr>
<tr><th>AA-EQS</th><th>MAC-EQS</th></tr>
<tr><td>Y-7</td><td>-</td><td>-</td><td>-</td><td>-</td><td rowspan="3">Agricultural Source:
- Walnut Farmland: 3664 da
- Cherry Farmland: 445 da
Industrial Source:
- Not Exist</td></tr>
<tr><td>Y-8</td><td>Fenpropimorph</td><td>79</td><td>-</td><td>12.5</td></tr>
<tr><td>Y-9</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
</table>

As it is depicted in Figure 3.15, the fenpropimorph fungicide was observed only in April sampling period. When the fungicide usage schedules of the pre-determined dominant crops of Reşadiye were assessed, it was seen that the month of April is the fungicide spraying period for the cherry and walnut crops raised in Reşadiye (Personal Communication with the Agricultural Engineers of Reşadiye District Directorate of Agriculture and Forestry, 2019). Based on the temporal relation between the local fungicide spraying schedule of Reşadiye and the EQS exceedance period of the fungicide observation at the Y-8 sampling station of the district, 3664 da walnut and 445 da cherry croplands located in Reşadiye were determined as the potential sources to be accountable for the fenpropimorph pollution at the Y-8 sampling station in Reşadiye.

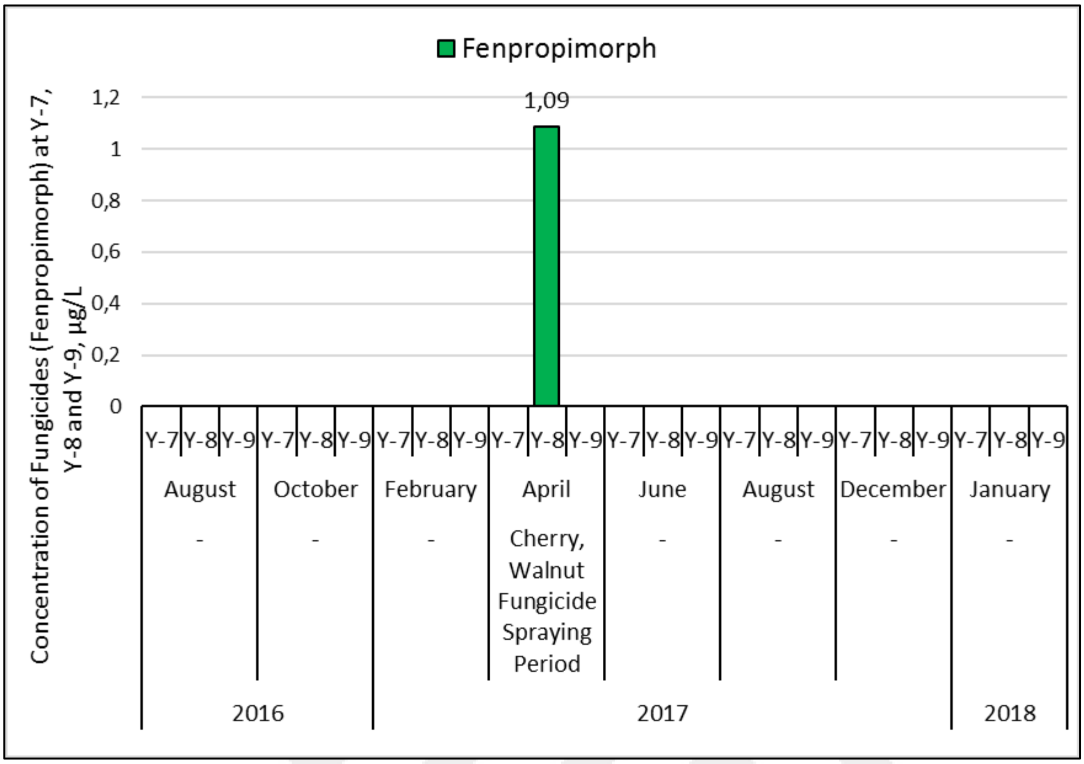

Figure 3.15 Correlation Between EQS Exceedance Months of Fungicides (at Y-7, Y-8 and Y-9) and Fungicide Spraying Periods for the Dominant Crops of Reşadiye

3.4.4.4.2 Niksar District (Y-10 and Y-39 Sampling Stations)

The Niksar District comprises various microclimates, which enable favorable environment for the growth of different types of agricultural products in the district. The Niksar Plain in the district embodies intense agricultural activities that implement irrigation-based farming. The economy of Niksar is primarily based on the industrial facilities that process agricultural and forestry products. The agriculture-based economic income of the district is mainly provided by the cultivation of grains, walnut, grape, potato and bean products (Personal Communication with the Agricultural Engineers of Niksar District Directorate of Agriculture and Forestry, 2019). As it is given in Table 3.20, the wheat fields were calculated as covering 56% of total agricultural land of Niksar, while the remaining 44% of the farmlands of the district was determined as being occupied by the various field crops, vegetables and fruit trees. The crops colored with red in Table 3.20 were defined as the dominant crops of the district, which consist of wheat, maize, alfalfa, bean, potato, grape, walnut, melon, rye, oat, spinach and cabbage. As it can be seen from the table, all these crops have considerably high areal shares among the other districts of the entire basin.

Table 3.20 The Calculated Percentage Shares of the Crop Areas in the Niksar District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Niksar District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Wheat	165451	**56**	**5.6**
Maize	34627	**12**	**11.8**
Barley	13417	4	1.7
Alfalfa	12500	4	**5.2**
Bean	11832	4	**20.5**
Potato	8500	3	**19.4**
Grape	6854	2	**9.3**
Walnut	6000	2	**13.1**
Triticale	5017	1	3.8
Onion	4660	1	4.1
Sugarbeet	4032	1	2.4
Sunflower	3867	1	1.0
Melon	4200	1	**28.4**
Chickpea	2800	1	1.7
Rye	1369	0.5	**29.2**
Oat	1022	0.3	**6.9**
Tomato	1015	0.3	1.4
Pepper	808	0.3	2.7
Spinach	500	0.2	**5.7**

Table 3.20 (cont'd)

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Niksar District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Tobacco	500	0.2	2.3
Cabbage	460	0.2	**12.0**
Aubergine	457	0.2	4.6
Apple	400	0.1	1.4
Lettuce	400	0.1	3.1
Other Crops	Negligibly Small Portion		

3.4.4.4.2.1 Determination of the Potential Sources of Insecticide Pollution at the Y-10 and Y-39 Sampling Stations of Niksar

When Table 3.21 is examined, it can be seen that dichlorvos was detected as the only insecticide that exceeds the EQS values at the Y-10 and Y-39 sampling stations of Niksar. As it is shown in Figure 3.16, the concentration of dichlorvos insecticide was observed as above its EQS values only in August and October sampling periods; whereas, in these two months, there is no insecticide spraying implementation for any of the dominant crops of the district. The agricultural engineers of Niksar District Directorate of Agriculture and Forestry (2019) reported that the insecticide usage schedules of the dominent crops of Niksar do not encompass the months of August and October. When the insecticide spraying schedules of the crops raised in Niksar were examined, it was seen that the most intense insecticide usage in the district is performed in July (Personal Communication with the Agricultural Engineers of Niksar District Directorate of Agriculture and Forestry, 2019).

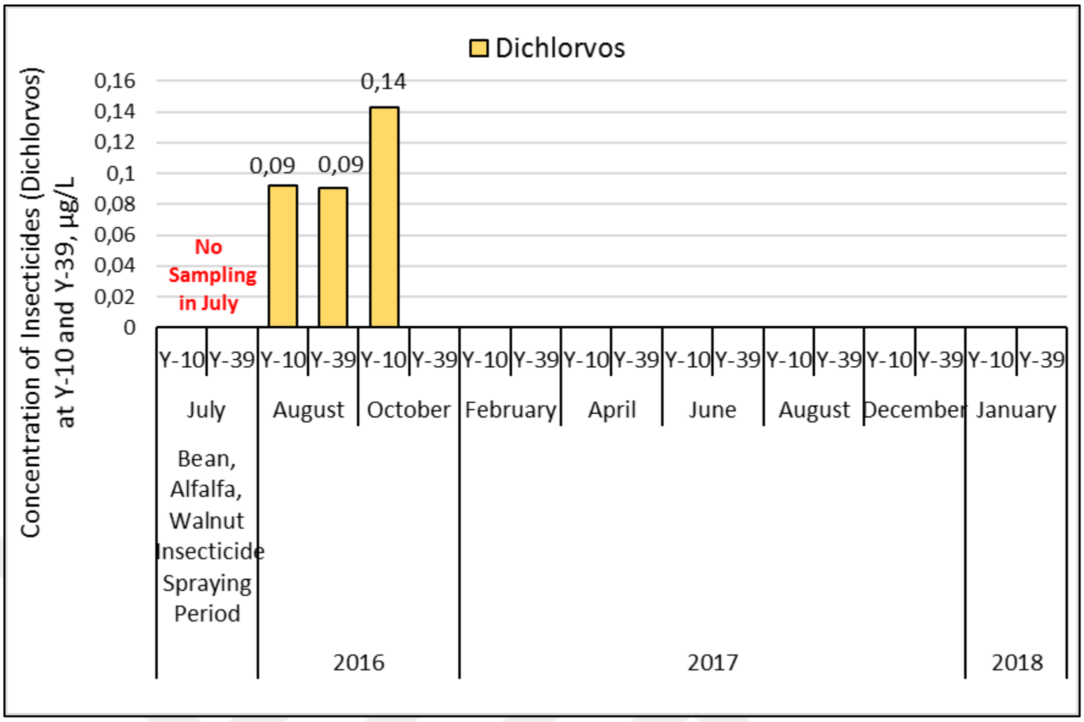

Figure 3.16 Correlation Between EQS Exceedance Months of Insecticides (at Y-10 and Y-39) and Insecticide Spraying Periods for the Dominant Crops of Niksar

As it is illustrated in Figure 3.16, in the month of July, three dominant crops of the district, which are alfalfa, bean and walnut were sprayed by the insecticides in Niksar. However, the water quality measurements for July are not available due to the absence of the sampling studies in this month. Therefore, the degree and type of insecticide pollution in July are not known; however, it was clearly observed that the insecticides detected at the sampling stations of Niksar exceeded their EQS values mainly in August and October with high exceedance levels. In this respect, the intense insecticide spraying activities performed in July for 12500 da alfalfa, 8116 da bean and 6000 da walnut croplands of Niksar were identified as the potential sources to contribute to the dichlorvos pollution observed in the following months of July (August and October) at the Y-10 and Y-39 sampling stations of the district.

Table 3.21 Potential Sources and Detection Percentages of the Insecticides Observed at the Y-10 and Y-39 Sampling Stations of Niksar

Stations	**Insecticides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Insecticides**
		AA-EQS	**MAC-EQS**		
Y-10	Dichlorvos	4817	20286	25	**Agricultural Source:** - Alfalfa Farmland: 12500 da - Bean Farmland: 8116 da - Walnut Farmland: 6000 da **Industrial Source:** - Wastewater Discharges of Agriculture and Food Industry in Niksar
Y-39	Dichlorvos	1829	12874	12.5	

When the existence of the industrial facilities in Niksar that integrate pesticide usage in their processes or use raw materials contaminated by the pesticides are examined, it was revealed that the Niksar District embodies the agricultural product and food processing industry (Niksar Öz-Bağ Agricultural Products and Food Industry), which discharges its wastewater into the river within the boundaries of the district. This facility manufactures tomato paste, grape leaves, fruit jams and grape molasses, which all have the high potential to be exposed to the pesticides and to contaminate the water body via wastewater discharges. Thus, the wastewater discharge of the agriculture and food industry located in Niksar has also a potential to be responsible for the dichlorvos pollution observed at the Y-10 and Y-39 sampling stations of Niksar.

3.4.4.4.2.2 Determination of the Potential Sources of Herbicide Pollution at the Y-10 and Y-39 Sampling Stations of Niksar

As presented in Table 3.22, aclonifen and ethalfluralin were determined as the herbicide types that exceed their MAC-EQS values at the sampling stations of Niksar. The concentration of aclonifen was calculated as above its MAC-EQS value with 160% and 371% exceedances at the Y-10 and Y-39 sampling stations, respectively. On the other hand, ethalfluralin was observed only at the Y-39 sampling station with 178% exceedance. As it is depicted in Figure 3.17, the exceedances of the EQS values by the aclonifen and ethalfluralin herbicides were observed in the October and April sampling periods, respectively. Among the pre-determined dominant crops of Niksar, potato, melon and grape crops have the herbicide spraying schedules that are implemented in the month of April (Personal Communication with the Agricultural Engineers of Niksar District Directorate of Agriculture and Forestry, 2019). As given in Table 3.20, it was calculated that the cultivation lands occupied by the potato, melon and grape crops in Niksar have substantially large areal shares with 19.4%, 28.4% and 9.3%, respectively, among their areas in the other districts of the basin. The high areal contributions of potato, melon and grape crops to the land use at the basin scale also makes these crops the major candidates as the sources of the April observations of the ethalfluralin herbicide.

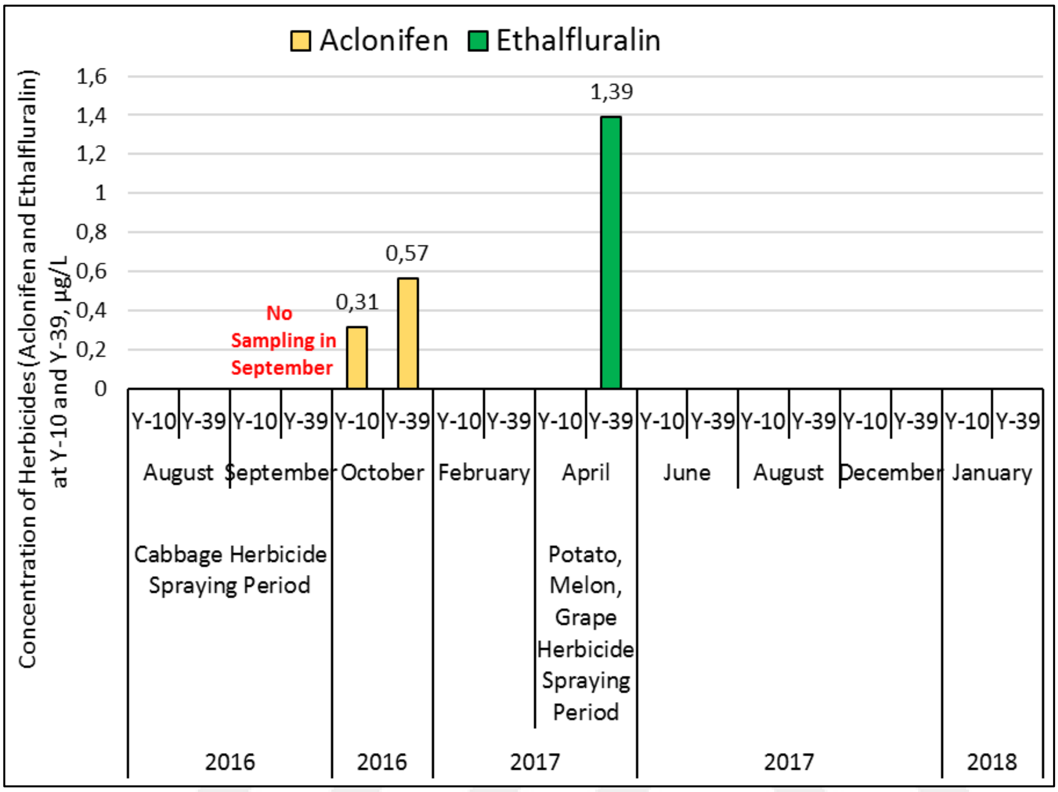

Figure 3.17 Correlation Between EQS Exceedance Months of Herbicides (at Y-10 and Y-39) and Herbicide Spraying Periods for the Dominant Crops of Niksar

When it comes to the October observations of herbicides, the agricultural engineers of Niksar District Directorate of Agriculture and Forestry (2019) stated that there is no herbicide application in Niksar in the month of October. On the other hand, as shown in Figure 3.17, August and September as the previous months of October are the main herbicide spraying periods for the cabbage crop, which is one of the pre-determined dominant crops of Niksar. In this regard, it was figured out that the EQS exceedances of the aclonifen herbicide observed in October strongly point out the herbicide spraying activities of the cabbage crops as being a potential source of the aclonifen pollution. When the precipitation regime of Niksar is taken into consideration, it was revealed that the monthly average precipitation amounts of August, September and October in Niksar are 20 mm, 38 mm and 77 mm, respectively (Meteoblue Climate History in Niksar, 2019). With respect to this precipitation trend, it was deduced that the herbicides sprayed in August and

September are prone to be washed and transported to the river with the sudden increase (from 38 mm to 77 mm) in the precipitation event that occurred in October. Hence, the effects of the August and September herbicide spraying practices on the river pollution can be seen in the late periods like October, when the precipitation events reach higher intensity compared to the previous months. By taking into account the local precipitation regime of Niksar, it was determined that the increasing precipitation pattern of the district is also compatible with the upward trend of the ethalfluralin concentration at the Y-39 sampling station. As a result of all these assessments, 460 da cabbage farmland cultivated in Niksar was determined as the potential source of the aclonifen pollution; besides, 8500 da potato, 6854 da grape and 4200 da melon farmlands of the district were identified as the potential sources of the ethalfluralin pollution.

Table 3.22 Potential Sources and Detection Percentages of the Herbicides Observed at the Y-10 and Y-39 Sampling Stations of Niksar

<table>
<tr><th rowspan="2">Stations</th><th rowspan="2">Herbicides</th><th colspan="2">EQS Exceedance %</th><th rowspan="2">Detection Frequency %</th><th rowspan="2">Potential Sources of the Observed Herbicides</th></tr>
<tr><th>AA-EQS</th><th>MAC-EQS</th></tr>
<tr><td>Y-10</td><td>Aclonifen</td><td>-</td><td>160</td><td>12.5</td><td rowspan="2">Agricultural Source:
- Cabbage Farmland: 460 da
Industrial Source:
- Wastewater Discharges of Agriculture and Food Industry in Niksar</td></tr>
<tr><td rowspan="2">Y-39</td><td>Aclonifen</td><td>-</td><td>371</td><td>12.5</td></tr>
<tr><td>Ethalfluralin</td><td>-</td><td>178</td><td>12..5</td><td>Agricultural Source:
- Potato Farmland: 8500 da
- Grape Farmland: 6854 da
- Melon Farmland: 4200 da
Industrial Source:
- Wastewater Discharges of Agriculture and Food Industry in Niksar</td></tr>
</table>

3.4.4.4.2.3 Determination of the Potential Sources of Fungicide Pollution at the Y-10 and Y-39 Sampling Stations of Niksar

The fungicide-type pesticide pollution was not observed at any of the Y-10 and Y-39 sampling stations of the Niksar District.

3.4.4.4.3 Merkez District (Y-11 Sampling Station)

In the Merkez District of the Tokat Province, animal husbandry, agricultural and industrial activities have all widespread applications with a high economic yield. The agricultural land use in the district is mainly composed of the cultivation of the field crops like potato, onion, maize and grains rather than horticultural crops like fruit trees and garden plants. The predominance of the field crops in the district brings about the abundance of weed infestations, which typically occur on the field-type crops (OKA Tokat Merkez District Report, 2018; Personal Communication with the Agricultural Engineers of Tokat Provincial Directorate of Agriculture and Forestry, 2019). As it is provided in Table 3.23, it was calculated that the field crops cultivated in the Merkez District, which mainly comprise barley, wheat, alfalfa, chickpea, sugarbeet, maize, onion, garlic, sainfoin and potato, are responsible for 77% of the total agricultural land use in the district. The remaining 23% of the agricultural land use in the district consists of the various garden plants and fruit trees with small cultivation areas.

Table 3.23 The Calculated Percentage Shares of the Crop Areas in the Merkez District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Merkez District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Barley	80972	**21**	**10.3**
Wheat	67373	**17**	2.3
Alfalfa	53500	**14**	**22.1**
Chickpea	30000	**8**	**18.5**
Sugarbeet	25583	**7**	**15.0**
Grape	22561	**6**	**30.7**
Maize	12955	3	4.4
Bean	9500	3	**16.5**
Onion	9240	2	**8.1**
Tomato	8315	2	**11.7**
Garlic	8000	2	**79.0**
Peach	7884	2	**36.0**

Table 3.23 (cont'd)

Agricultural Crop	Area of Agricultural Land, decare (TurkStat, 2020)	Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Merkez District, %	Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %
Sainfoin	6500	2	**13.6**
Apple	6416	2	**23.0**
Sweet Cherry	4600	1	**12.0**
Potato	4500	1	**10.3**
Lettuce	4447	1	**34.3**
Cucumber	3686	1	**22.8**
Sour Cherry	3200	0.8	**59.0**
Walnut	3200	0.8	**7.0**
Pepper	2810	0.7	**9.5**
Spinach	2250	0.6	**25.5**
Pear	2000	0.5	**42.0**
Oat	1874	0.5	**13.0**
Triticale	2598	0.7	2
Aubergine	760	0.2	**7.6**
Cabbage	720	0.2	**18.8**
Lentil	301	0.1	1.2
Sunflower	181	0.05	0.05
Other Crops	Negligibly Small Portion		

3.4.4.4.3.1 Determination of the Potential Sources of Insecticide Pollution at the Y-11 Sampling Station of Merkez

The insecticide-type pesticide pollution was not observed at the Y-11 sampling station of the Merkez District.

3.4.4.4.3.2 Determination of the Potential Sources of Herbicide Pollution at the Y-11 Sampling Station of Merkez

As it is presented in Table 3.24, the herbicide group was determined as the only pesticide type that exceeds the EQS values at the Y-11 sampling station of the Merkez District. The concentrations of the aclonifen and ethalfluralin herbicides were calculated as above their MAC-EQS values with 212.9% and 105.8% exceedances, respectively, at the Y-11 sampling station of the Merkez District.

As it was mentioned, for the field-type crops, the weed infestation is the major issue that is required to be controlled and mitigated by the herbicide spraying activities. The agricultural engineers of Tokat Provincial Directorate of Agriculture and Forestry (2019) specified that the field crops raised in the district require intense herbicide usage due to the severe weed attacks on these field crops. Since the field crops raised in the district were determined as being responsible for the remarkably high areal portion of the agricultural land use in the district, the EQS exceedances of the aclonifen and ethalfluralin herbicides were strongly correlated with the herbicide usage profile of the dominant crops of the Merkez District. The compliance between the EQS exceedance periods of the herbicides at the Y-11 sampling station and the herbicide application months of the dominant crops of the district was given in Figure 3.18. As it is provided in Figure 3.18, the EQS exceedances of the aclonifen and ethalfluralin herbicides were observed in the October and April sampling periods, respectively. When the herbicide spraying schedules of the dominant crops of the Merkez District were examined, it was revealed that October is the month of herbicide spraying activities for the grains like wheat and barley crops cultivated in the district. On the other hand, the month of April is the month of herbicide spraying activities for the onion, garlic, chickpea, sugarbeet, cherry, peach, apple and grape crops raised in the district (Personal Communication with the Agricultural Engineers of Tokat Provincial Directorate of Agriculture and Forestry, 2019). As it can be figured out from the herbicide spraying periods of the district, the herbicide applications of almost all of the dominant crops in the district are performed in April.

As it is given in Table 3.23, it was calculated that garlic, cherry, peach, grape, apple, chickpea, sugarbeet and onion crops account for 79%, 59%, 36%, 31%, 23%, 19%, 15% and 8% of the total areas of the same type crops raised the other districts of the basin, respectively. These basin-wide areal shares of the garlic, cherry, peach, grape, apple, chickpea, sugarbeet and onion crops constitute a considerably large portion of the crop cultivation lands of the basin. In this respect, their contribution to the herbicide pollution observed within the boundaries of Merkez can be seen as inevitable due to the spatial and temporal compatibility between the herbicide usage trend of the district and the herbicide detections at the Y-11 sampling station of the district. In the view of all these evaluations, 80972 da barley and 67373 da wheat farmlands were identified as a potential source of the ethalfluralin observation at the Y-11 sampling station; moreover, 30000 da chickpea, 25583 da sugarbeet, 9240 da onion, 8000 da garlic, 22561 da grape, 7800 da cherry, 7884 peach and 6416 da apple farmlands were determined as the potential sources of the aclonifen pollution observed at the Y-11 sampling station of the Merkez District.

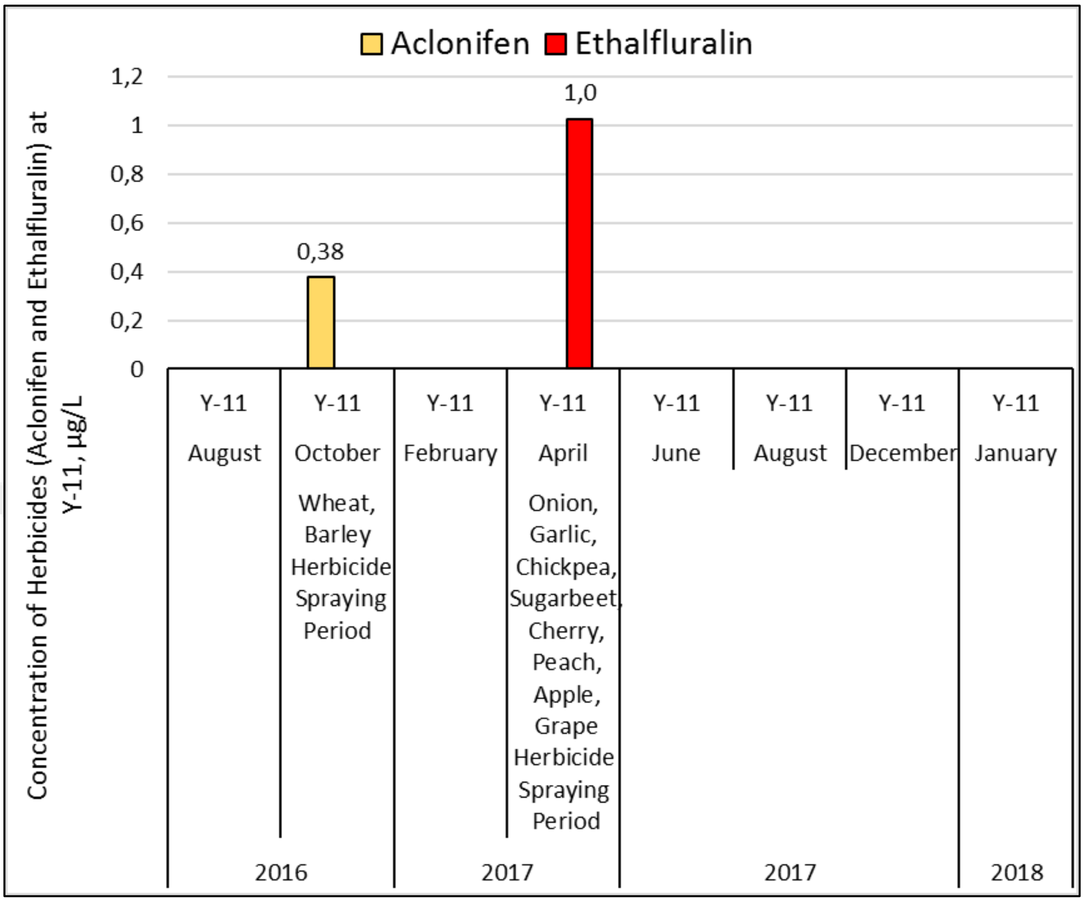

Figure 3.18 Correlation Between EQS Exceedance Months of Herbicides (at Y-11) and Herbicide Spraying Periods for the Dominant Crops of Merkez

The Merkez District embodies the variety of agricultural and food industries that use pesticides during the different steps of the production or raw materials exposed to the pesticides. Dimes Food and Beverage Industry, Er-Pa Agricultural Products Industry, Tokat Topçam Food Production, Mufi Food Production are some of the industries located in the Merkez District. In total, the food production and agriculture-related 11 industries that discharge their wastewater into the Yeşilırmak River Basin exist within the boundaries of the Merkez District. Due to the abundance of these industries located in the Merkez District, there are lots of industrial sources that have the potential to contribute to the herbicide pollution within the boundaries of this district.

Table 3.24 Potential Sources and Detection Percentages of the Herbicides Observed at the Y-11 Sampling Stations of Merkez

<table>
<tr><th rowspan="2">Stations</th><th rowspan="2">Herbicides</th><th colspan="2">EQS Exceedance %</th><th rowspan="2">Detection Frequency %</th><th rowspan="2">Potential Sources of the Observed Herbicides</th></tr>
<tr><th>AA-EQS</th><th>MAC-EQS</th></tr>
<tr><td rowspan="2">Y-11</td><td>Aclonifen</td><td>-</td><td>212.9</td><td>12.5</td><td>Agricultural Source:
-Chickpea: 30000da
- Sugarbeet: 25583 da
- Onion: 9240 da
- Garlic: 8000 da
- Grape : 22561 da
- Peach, Cherry, Apple Trees
Industrial Source:
- Wide range of food, beverage and agricultural industries</td></tr>
<tr><td>Ethalfluralin</td><td>-</td><td>105.8</td><td>12.5</td><td>Agricultural Source:
- Barley Farmland: 80972 da
- Wheat Farmland: 67373 da
Industrial Source:
- Wide range of food, beverage and agricultural industries</td></tr>
</table>

3.4.4.4.3.3 Determination of the Potential Sources of Fungicide Pollution at the Y-11 Sampling Station of Merkez

The fungicide-type pesticide pollution was not observed at the Y-11 sampling station of the Merkez District.

3.4.4.4.4 Almus District (Y-12 and Y-13 Sampling Stations)

In the Almus District, the diversity of the agricultural products is relatively less compared to the other districts of the Tokat Province. Among the eight districts of Tokat, where sampling stations are located, the Almus District has the second highest altitude with 853 m after the Sulusaray district, which has a 1035 m altitude. Animal husbandry activities are the primary source of the economic income of the district. Correspondingly, agricultural activities and agrochemical spraying practices are not prevalent in this district. The existing agricultural activities of the district is limited to the forage cultivation that includes the grain and pasture fields (Personal Communication with the Agricultural Engineers of Almus District Directorate of Agriculture and Forestry, 2019). As it is presented in Table 3.25, it was calculated that the grain and pasture areas of Almus, which comprise wheat, alfalfa, barley and sainfoin fields, occupy 87% of the total agricultural land in the district. The remaining 13% of the total agricultural area in the district consists of small and separate vegetable and fruit orchards. According to the agricultural engineers of Almus District Directorate of Agriculture and Forestry (2019), the forage-type crops in Almus are not sprayed by the insecticides because the stink bugs, the typical invasive insect species of the grain fields, do not exist in this district. In this respect, it was figured out that 87% of the agricultural lands (grain and pasture areas) in Almus are not exposed to insecticide-type pesticides. Regarding the herbicide and fungicide usage in Almus, the agricultural engineers of Almus District Directorate of Agriculture and Forestry (2019) emphasized that the spraying activities of the herbicides and fungicides on the forage fields in Almus are rare or entirely absent due to the small cultivation areas and low diversity of the agricultural crops raised in the district .

Table 3.25 The Calculated Percentage Shares of the Crop Areas in the Almus District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Almus District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Wheat	26988	**35**	0.9
Alfalfa	25000	**33**	**10.3**
Barley	10415	**14**	1.3
Sainfoin	3500	**5**	**7.3**
Chickpea	2000	3	**1.2**
Sugarbeet	1637	2	1.0
Bean	1580	2	2.7
Walnut	1160	2	2.5
Sour Cherry	480	0.6	**8.8**
Potato	450	0.6	1.0
Other crops	Negligibly Small Portion		

As it is stated in Table 3.26, the concentrations of the dichlorvos and diflubenzuron insecticides, and the HCB fungicide were calculated as above their EQS values at the sampling stations of Almus. It was determined that among these three pesticides, only dichlorvos exceeded both of its AA-EQS and MAC-EQS values at both Y-12 and Y-13 sampling stations of the district. On the other hand, diflubenzuron and HCB exceeded only their MAC-EQS values with 96% and 95%, respectively, only at the Y-12 sampling station. As it can be seen in Table 3.26, dichlorvos is the prevailing pesticide of the sampling stations in Almus because dichlorvos have significantly higher EQS exceedance values compared to HCB and diflubenzuron. Regarding the pollution that stems from the agrochemical usage against weeds, the herbicide-type pesticides were not observed at the Y-12 and Y-13 sampling stations of Almus.

Table 3.26 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-12 and Y-13 Sampling Stations of Almus

Stations	**Pesticides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Pesticides**
		AA-EQS	**MAC-EQS**		
Y-12	Diflubenzuron	-	96	12.5	**Agricultural Source:** - Not Exist **Industrial Source:** - The Wastewater Discharges of Vegetable and Ground Cereal Production Facility
	Dichlorvos	4064	15192	25	
	HCB	-	95	25	
Y-13	Dichlorvos	1974	13873	12.5	

All in all, dichlorvos, diflubenzuron and HCB were identified as the three pesticides that raise concern for the water quality in the boundaries of Almus. As it was mentioned, agrochemical usage is not common agricultural practice in Almus; hence, the existence of these three pesticides can not be attributed to the agricultural land use of the district. In this respect, the industrial facilities of Almus that have the potential to contribute to the pesticide pollution were taken into consideration for the source identification of the pesticides. Regarding the industrial activities associated with the pesticide usage, it was revealed that Kalenderoğlu Food Industry located in the Almus District discharges its wastewater into the Yeşilırmak River Basin. In this facility, the processing of the vegetables and ground cereals, which have a high potential to be exposed to the various types of pesticides, is carried out as the main operation of the facility. Since the wastewater of this facility is discharged to the Yeşilırmak River, the discharges of this industry were identified as the candidate to be the potential source of the pesticide pollution observed at the sampling stations of Almus.

3.4.4.4.5 Pazar District (Y-14 Sampling Station)

The Pazar District is located on Kazova Plain, which embodies productive soil and provides favorable lands for farming activities. The agricultural sector has an important place in the economy of Pazar (OKA Pazar District Report, 2018). As it is provided in Table 3.27, maize, wheat, tomato, sunflower, sugarbeet, alfalfa, bean, pepper and melon were identified as the dominant crops of Pazar with the areal shares above 5% at the district scale and/or the basin scale. Among these crops, it was determined that tomato has a substantially high areal share by being responsible for 21% of the total tomato cultivation performed in the entire basin. According to the agricultural engineers of Pazar District Directorate of Agriculture and Forestry (2019), the tomato crops raised in Pazar have a quite intense pesticide spraying schedule in terms of both quantity and frequency of the pesticide application. Due to the long vegetation period of tomato, the agricultural spraying of tomato requires a considerably long application period. Thus, the pesticide spraying schedule of the tomato crop raised in the Pazar District encompasses a wide period of time (Personal Communication with the Agricultural Engineers of Pazar District Directorate of Agriculture and Forestry, 2019).

Table 3.27 The Calculated Percentage Shares of the Crop Areas in the Pazar District

Agricultural Crop	Area of Agricultural Land, decare (TurkStat, 2020)	Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Pazar District, %	Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %
Maize	24576	**25**	**8.4**
Wheat	19069	**19**	0.6
Tomato	14920	**15**	**21**
Sunflower	9691	**10**	2.6
Sugarbeet	9210	**9**	**5.4**
Alfalfa	4500	**5**	1.9

Table 3.27 (cont'd)

Agricultural Crop	Area of Agricultural Land, decare (TurkStat, 2020)	Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Pazar District, %	Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %
Bean	3600	4	**6.2**
Grape	3311	3	4.5
Pepper	2050	2	**6.9**
Barley	1642	2	0.2
Melon	1600	2	**10.8**
Walnut	720	1	1.2
Cucumber	661	1	4.1
Apple	634	1	2.3
Chickpea	501	1	0.3
Other Crops	Negligibly Small Portion		

3.4.4.4.5.1 Determination of the Potential Sources of Insecticide Pollution at the Y-14 Sampling Station of Pazar

As it is given in Table 3.28, diflubenzuron was determined as the only insecticide that exceeded it EQS values at the Y-14 sampling station of the Pazar District. The concentration of diflubenzuron was calculated as above only its MAC-EQS value with 148% exceedance in one observation out of eight sampling periods corresponding to 20% detection frequency. As it is demonstrated in Figure 3.19, the EQS exceedance of diflubenzuron was observed only in the October sampling period. When the insecticide application months of the dominant crops of Pazar, which were reported by the agricultural engineers of Pazar District Directorate of Agriculture and Forestry (2019), are taken into consideration, it was revealed that the month of October is not responsible for the insecticide spraying of any pre-determined dominant crops of the district. The agricultural engineers of Pazar

District Directorate of Agriculture and Forestry (2019) specified that almost all of the insecticide spraying activities of Pazar are performed between the months of June and September. September is the month of insecticide spraying for the tomato crops, which are known to be exposed to the most intense use of pesticides in Pazar compared to the other dominant crops raised in the district. The insecticide spraying of tomato fields of Pazar is also carried out in August. The month of August is also responsible for the insecticide spraying practices of the bean, sugarbeet and melon crops of Pazar (Personal Communication with the Agricultural Engineers of Pazar District Directorate of Agriculture and Forestry, 2019). As it can be understood from the insecticide usage schedule of Pazar, most of the dominant crops raised in the district are sprayed by insecticides in the month of August. However, in the August sampling period, the insecticide-type pesticides were not observed at the sampling stations of the district. The incompatibility between the absence of insecticide pollution in the August sampling period and the presence of the intense insecticide usage in August can be linked with the remarkably low amount of precipitation in Pazar in the month of August. According to the district-specific precipitation data reported by Meteoblue Climate History Database (2019), August is the least rainy month of Pazar with 3 mm monthly average precipitation amount. In the month of September, the average precipitation in Pazar is still low in amount with 8 mm. Whereas, in the month of October, the average precipitation amount of the district drastically increases to 30 mm. Since the relative precipitation amounts in August and September are considerably lower than in October, the wash and transport of the pesticides from the application area to the river are expected to take place in October under the impact of the sharply increasing rainfall trend in this month. Therefore, the impact of the insecticide spraying activities performed in August and September tends to emerge in October. In this regard, the insecticide spraying of tomato, bean, sugarbeet and melon crops in the months of August and September have quite high potential to contribute to the insecticide pollution observed in the October sampling period with the drastic increase in the precipitation amount in October. As a result of all these assessments, 14920 da tomato, 9210 da sugarbeet, 3600 da bean and 1600 da melon farmlands of the Pazar District were identified as the potential sources of the diflubenzuron pollution observed at the Y-14 sampling station of the district.

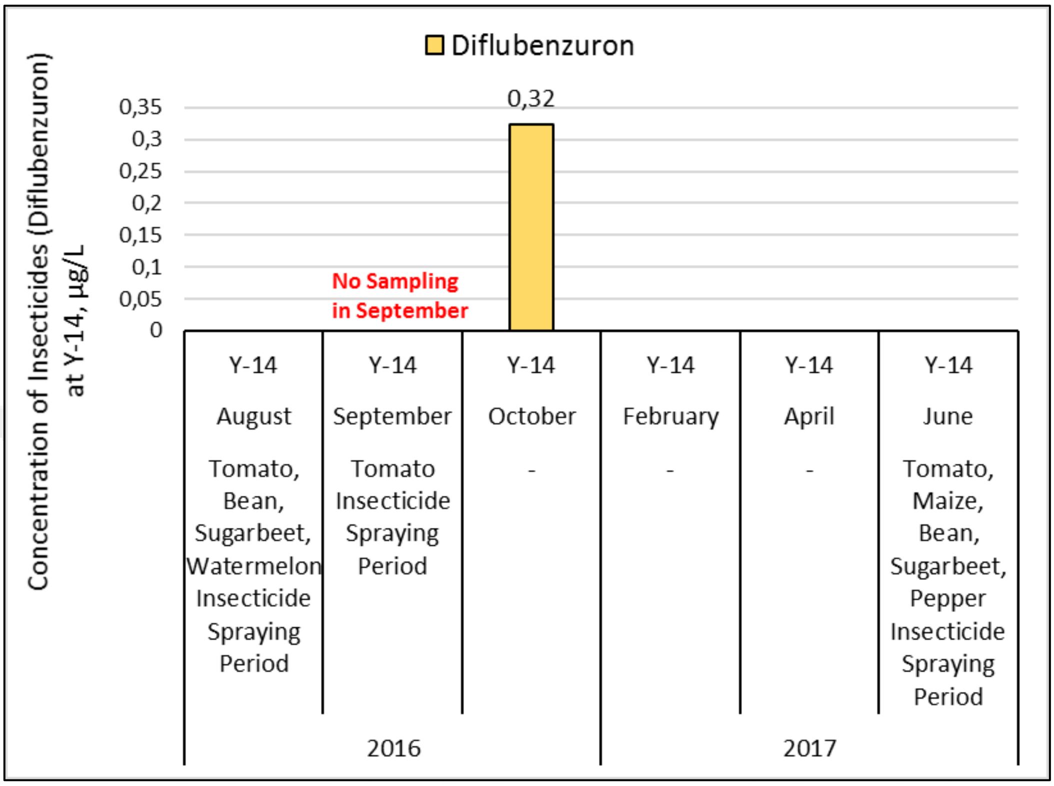

Figure 3.19 Correlation Between EQS Exceedance Months of Insecticides (at Y-14) and Insecticide Spraying Periods for the Dominant Crops of Pazar

When the industrial facilities that have potential to be the source of the observed pesticide pollution were examined, it was seen that ground grain, flour, vegetable products and mixed animal feed production facility (Akar Flour and Agricultural Product Industry) is the only industry that uses pesticides in their processes and discharges its wastewater to the river within the boundaries of the Pazar District.

Table 3.28 Potential Sources and Detection Percentages of the Insecticides Observed at the Y-14 Sampling Station of Pazar

Stations	Insecticides	EQS Exceedance %		Detection Frequency %	Potential Sources of the Observed Insecticides
		AA-EQS	MAC-EQS		
Y-14	Diflubenzuron	-	148	20	**Agricultural Source:** - Tomato : 14920 da - Sugarbeet : 9210 da - Bean: 3600 da - Melon: 1600 da **Industrial Source:** - The Wastewater Discharges of the Mixed Animal Feed Industry

3.4.4.4.5.2 Determination of the Potential Sources of Herbicide Pollution at the Y-14 Sampling Station of Pazar

As it is provided in Table 3.29, aclonifen and ethalfluralin were observed as the herbicide-type pesticides of the Y-14 sampling station of the Pazar District. While the concentration of aclonifen was calculated as above both of its AA-EQS and MAC-EQS values with 9% and 437% exceedances, respectively, the concentration of ethalfluralin was calculated as above only its MAC-EQS with 94% exceedance. As can be seen in Figure 3.20, it was determined that aclonifen and ethalfluralin herbicides exceeded their EQS values in October and April, respectively. The agricultural engineers of the Pazar District Directorate of Agriculture and Forestry (2019) reported that, in the months of October, September and August, there is no herbicide spraying activity for any dominant crop raised in the Pazar District. Due to the absence of herbicide spraying activities in October and, also in September and August, being previous months, the aclonifen pollution observed in October was not associated with the agricultural land use in the Pazar District. Regarding the industrial sources of the herbicide pollution in the Pazar District, the wastewater discharges from the mixed animal feed industry located in the district, which was mentioned in the previous section, has the potential to be responsible for the aclonifen pollution observed at the Y-14 sampling station.

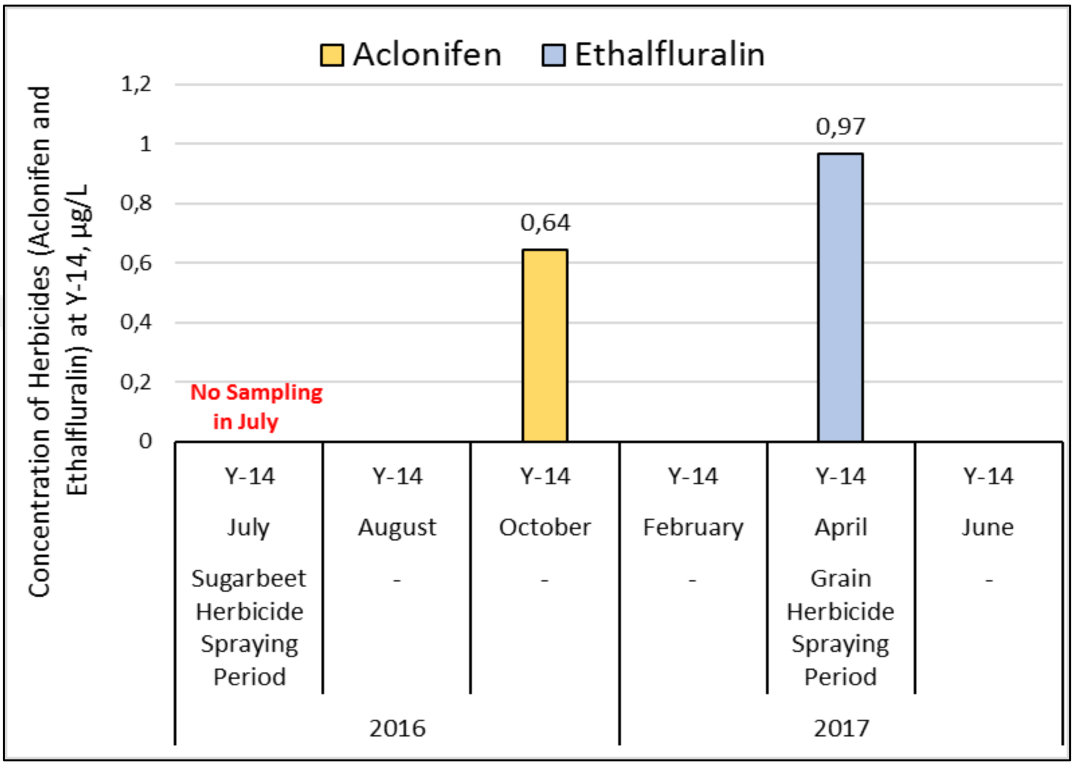

Figure 3.20 Correlation Between EQS Exceedance Months of Herbicides (at Y-14) and Herbicide Spraying Periods for the Dominant Crops of Pazar

As it is shown in Figure 3.20, the concentration of the ethalfluralin herbicide was calculated as above its EQS value only in the April sampling period. In the month of April, the grain crops like wheat and barley are sprayed by the herbicides in the Pazar District (Personal Communication with the Agricultural Engineers of Pazar District Directorate of Agriculture and Forestry, 2019). Among the dominant crops of the Pazar District colored with red in Table 3.27, wheat was determined as the major grain-type crop of the district with a 19% areal share. Since the grain fields in Pazar, including wheat lands, require intense herbicide protection against the weed attacks in April, the wheat fields of the district have the high potential to contribute to the ethalfluralin pollution observed in the April sampling period. In this respect, the EQS exceedance of the ethalfluralin herbicide in April was attributed to the herbicide spraying activities of the wheat crop, which are mainly employed in April.

Table 3.29 Potential Sources and Detection Percentages of the Herbicides Observed at the Y-14 Sampling Station of Pazar

Stations	**Herbicides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Herbicides**
		AA-EQS	**MAC-EQS**		
Y-14	Ethalfluralin	-	94	20	**Agricultural Source:** - Wheat Farmland: 19069 da **Industrial Source:** - The Wastewater Discharges of the Mixed Animal Feed Industry
	Aclonifen	9	437	20	**Agricultural Source:** - Not Exist **Industrial Source:** - The Wastewater Discharges of the Mixed Animal Feed Industry

3.4.4.4.5.3 Determination of the Potential Sources of Fungicide Pollution at the Y-14 Sampling Station of Pazar

The fungicide-type pesticide pollution was not observed at the Y-14 sampling station of the Pazar District.

3.4.4.4.6 Sulusaray District (Y-16 Sampling Station)

The Sulusaray District has the highest altitude among the eight districts of Tokat with 1035 m. In parallel with the high altitude, Sulusaray embodies the harsh continental climate, which brings about the dominance of the grain fields as the primary agricultural lands of Sulusaray. In this regard, the diversity of the agricultural products raised in the district is limited to the forage-type crops (Personal Communication with the Agricultural Engineers of Sulusaray District Directorate of Agriculture and Forestry, 2019). As it is given in Table 3.30, it was determined that the forage lands, which include the grain fields (wheat, barley, oat and rye) and the pasture fields (alfalfa and sainfoin), are responsible for %87 of the total agricultural land use of Sulusaray. The remaining agricultural lands of the district are largely covered by the sugarbeet fields, which are responsible for 12% of the agricultural land use of the district. All in all, it was revealed that the forage areas and sugarbeet fields occupy nearly all agricultural areas of the district.

Table 3.30 The Calculated Percentage Shares of the Crop Areas in the Sulusaray District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Sulusaray District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Wheat	41673	**52**	1.4
Barley	18055	**23**	2.3
Sugarbeet	9722	**12**	**5.7**
Oat	5600	**7**	0.9
Alfalfa	2500	3	1.0
Sainfoin	500	1	1.0
Rye	228	1	4.9
Other crops	Negligibly Small Portion		

As presented in Table 3.31, the concentrations of dichlorvos, aclonifen and HCB were calculated as above their EQS values at the Y-16 sampling station of Sulusaray. It was observed that, among these three pesticides, both of the AA-EQS and the MAC-EQS values were exceeded only by dichlorvos at the Y-16 sampling station.

Unlike dichlorvos, the aclonifen and HCB pesticides exceeded only their MAC-EQS values with 229% and 20%, respectively. Therefore, it was identified that only dichlorvos constitutes a problem on an annual basis at the Y-16 sampling station. Regarding the detection frequencies of the observed pesticides, all of these three pesticides exceeded their EQS values in one observation out of eight sampling periods. The EQS exceedances of dichlorvos, aclonifen and HCB were observed in the August and October sampling periods. According to the pesticide spraying schedule of the grain crops, which is reported by the agricultural engineers of Sulusaray District Directorate of Agriculture and Forestry (2019), the herbicide spraying activities of the grain crops raised in Sulusaray are implemented in April and May, whereas the insecticide and fungicide sprayings are not carried out due to the absence of the insects and fungal origin infestations in the grain farmlands of the district. The pesticide spraying of sugarbeet fields is performed in March and April against insects; March, April and May against weeds; June and July against fungal diseases (Personal Communication with the Agricultural Engineers of Sulusaray District Directorate of Agriculture and Forestry, 2019). When the agricultural spraying periods of the sugarbeet and grain crops, which were determined as the dominant crops of the district, were taken into consideration, it was seen that the pesticide detection periods and the pesticide spraying periods in Sulusaray are incompatible with each other. Therefore, the existence of these pesticides above their EQS values at the Y-16 sampling station was not attributed to the agricultural land use of Sulusaray.

Table 3.31 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-16 Sampling Station of Sulusaray

<table>
<tr><th rowspan="2">Stations</th><th rowspan="2">Pesticides</th><th colspan="2">EQS Exceedance %</th><th rowspan="2">Detection Frequency %</th><th rowspan="2">Potential Sources of the Observed Pesticides</th></tr>
<tr><th>AA-EQS</th><th>MAC -EQS</th></tr>
<tr><td rowspan="3">**Y-16**</td><td>Dichlorvos</td><td>1548</td><td>10953</td><td>12.5</td><td rowspan="3">**Agricultural Source:**
- Not Exist
Industrial Source:
- The Wastewater Discharges of the Flour Production Facilities</td></tr>
<tr><td>Aclonifen</td><td>-</td><td>229</td><td>12.5</td></tr>
<tr><td>HCB</td><td>-</td><td>20</td><td>12.5</td></tr>
</table>

The Sulusaray District embodies various small flour production facilities, which typically use the grain crops as raw material (OKA Sulusaray District Report, 2018). According to the studies conducted by Randhawa, Ahmed, & Javed et al. (2014), numerous types of pesticides are used during the storage of grain crops in the grain processing facilities in order to protect these crops from the pest infestations like insect attacks and mold growths. Since the stored grains require long-term protection against the potential pest formations, the intensity of the pesticide use throughout the storage period is quite high in the food factories like flour and forage manufacture facilities. In this context, the EQS exceedances of the pesticides observed at the Y-16 sampling station were attributed to the wastewater discharges of the flour production industries located within the boundaries of the Sulusaray District.

3.4.4.4.7 Turhal District (Y-17 and Y-18 Sampling Stations)

In the Turhal District, agricultural activities play an effective role as being responsible for the considerable part of the economic income. The high intensity of the irrigation practices in the Turhal District enables farmers to grow the various types of agricultural products with high yields in the district. Tomato farming is one the most widely applied agricultural activity in the Turhal District with its extensive agrochemical usage practices (Personal Communication with the Agricultural Engineers of Turhal District Directorate of Agriculture and Forestry, 2019). As it can be seen in Table 3.32, it was calculated that the tomato areas in the district account for 27.1% of the total tomato fields cultivated in the entire basin. In addition to the tomato crop, the grain, sunflower, pepper, melon, aubergine and spinach plants were also identified as the dominant crops of the district.

Table 3.32 The Calculated Percentage Shares of the Crop Areas in the Turhal District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Turhal District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Wheat	214548	**58**	**7.2**
Sunflower	42768	**12**	**11.3**
Barley	25689	**7**	3.3
Tomato	19233	**5**	**27.1**
Maize	14901	4	**5.1**
Alfalfa	11200	3	4.6
Sugarbeet	8187	2	4.8
Onion	4100	1	3.6
Melon	4000	1	**27.1**
Pepper	3800	1	**13.0**
Grape	3461	0.9	4.7
Bean	2550	0.7	4.4
Chickpea	2500	0.7	1.5
Walnut	1950	0.5	4.3
Aubergine	1500	0.4	**15.5**
Apple	1045	0.3	3.7

Table 3.32 (cont'd)

Agricultural Crop	Area of Agricultural Land, decare (TurkStat, 2020)	Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Turhal District, %	Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %
Spinach	1000	0.3	**11.3**
Cucumber	768	0.2	4.8
Hash	708	0.2	4.3
Lentil	501	0.1	2.0
Potato	400	0.1	0.9
Cherry	345	0.1	0.9
Sainfoin	250	0.1	0.5
Lettuce	225	0.1	1.7
Pear	210	0.1	4.4
Other Crops	Negligibly Small Portion		

3.4.4.4.7.1 Determination of the Potential Sources of Insecticide Pollution at the Y-17 and Y-18 Sampling Stations of Turhal

As it is provided in Table 3.33, the concentrations of the dichlorvos, diflubenzuron, prothiofos and HCH insecticides were observed as above their EQS values at the sampling stations of the Turhal District. While the dichlorvos and diflubenzuron insecticides exceeded their EQS values at both of the Y-17 and Y-18 sampling stations, the HCH and prothiofos insecticides exceeded their EQS values only at the Y-18 sampling station. It was determined that, among these four insecticides, prothiofos has the lowest AA-EQS exceedance with 0.7% at the Y-18 sampling station. In contrast, dichlorvos has the highest AA-EQS exceedance with 3115% at the Y-17 sampling station. The relation between the EQS exceedance months of the insecticides and the insecticide spraying periods for the dominant crops of Turhal is demonstrated in Figure 3.21.

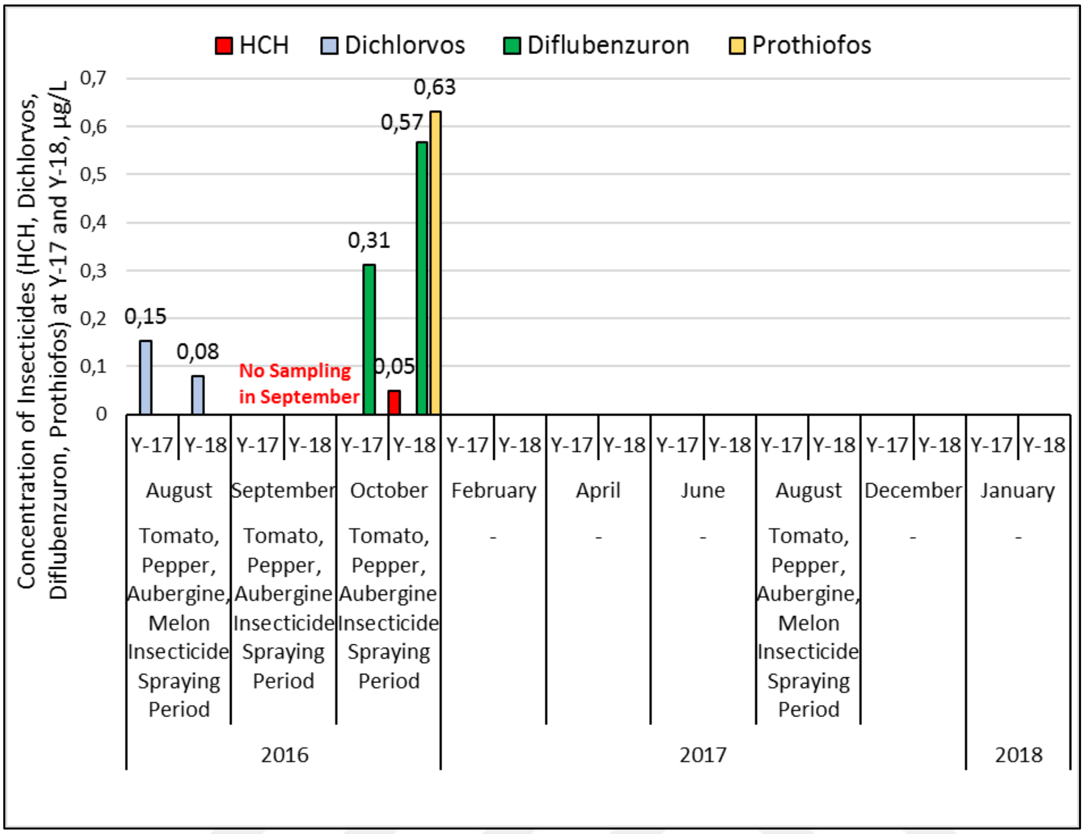

Figure 3.21 Correlation Between EQS Exceedance Months of Insecticides (at Y-17 and Y-18) and Insecticide Spraying Periods for the Dominant Crops of Turhal

As can be seen in Figure 3.21, the concentrations of the HCH, diflubenzuron and prothiofos insecticides were determined as above their EQS values only in the October sampling period. When the insecticide usage schedules of the dominant crops of Turhal are examined, it was revealed that the insecticide sprayings of the tomato, pepper and aubergine crops are carried out in all of August, September and October periods (Personal Communication with the Agricultural Engineers of Turhal District Directorate of Agriculture and Forestry, 2019). Even though the insecticide spraying period of the tomato, pepper and aubergine crops encompass all these three months, the diflubenzuron, prothiofos and HCH insecticides were observed only in October. In other words, there was not observed any EQS exceedance by these three insecticides in the months of August and September despite the presence of the insecticide spraying activities in Turhal in August, September and October. This discrepancy indicates that there exist driving forces that trigger the transport of the insecticides to the river in the month of October. One of the major driving force is the precipitation pattern of the district. According to the district-specific climate data reported by Meteoblue Climate History Database (2019), the monthly average precipitation amounts in the Turhal District for August, September and October are 3 mm, 8 mm and 30 mm, respectively. The spread of the pesticides from the farmlands to the non-target environments is not expected under the low precipitation conditions, which occur in the months of August and September in Turhal. The drastic increase in the amount of precipitation in October explains why the diflubenzuron, prothiofos and HCH insecticides were observed only in October despite the spraying activities performed in all of the August, September and October periods. As it is shown in Figure 3.21, different from the HCH, diflubenzuron and prothiofos insecticides, the concentrations of the dichlorvos insecticide was calculated as above its EQS values in the August sampling period, which is the insecticide spraying period for the melon, tomato, pepper and aubergine crops of Turhal. All these assessments point out that the EQS exceedances of the dichlorvos, HCH, diflubenzuron and prothiofos insecticides are strongly related to the insecticide spraying activities of the tomato, melon, pepper and aubergine crops, which are implemented in the months of August, September and October. In this context, 19233 da tomato, 4000 da melon, 3800 da pepper and 1500 da aubergine farmlands in Turhal were identified as the potential sources of the dichlorvos, HCH, diflubenzuron and prothiofos pollution observed at the Y-17 and Y-18 sampling stations of Turhal.

Table 3.33 Potential Sources and Detection Percentages of the Insecticides Observed at the Y-17 and Y-18 Sampling Stations of Turhal

Stations	Insecticides	EQS Exceedance %		Detection Frequency %	Potential Sources of the Observed Insecticides
		AA-EQS	MAC-EQS		
Y-17	Dichlorvos	3115	21697	12.5	**Agricultural Source:** - Tomato: 19233 da - Melon: 4000 da - Pepper: 3800 da - Aubergine: 1500 da **Industrial Source:** - The wastewater discharges of the agriculture industry-wheat, sunflower, sugarbeet, forage plants and fruit processing
	Diflubenzuron	-	139	12.5	
Y-18	Dichlorvos	1601	11317	12.5	
	HCH	-	21	12.5	
	Diflubenzuron	-	336	12.5	
	Prothiofos	0.73	-	12.5	

When the industrial sources of pesticide pollution were investigated, it was revealed that the agricultural enterprise facility (Kazova Vasfi Diren Agricultural Industry), which discharges its wastewater into the Yeşilırmak River Basin, is located within the boundaries of Turhal. In this facility, the various types of the agricultural crops are processed like wheat, sunflower, sugarbeet, forage plants and fruits, which are all highly likely to be exposed to pesticides. Hence, the wastewater discharges of this facility was also identified as one of the potential sources of the pesticide pollution observed at the Y-17 and Y-18 sampling stations of Turhal.

3.4.4.4.7.2 Determination of the Potential Sources of Herbicide Pollution at the Y-17 and Y-18 Sampling Stations of Turhal

As presented in Table 3.34, aclonifen was determined as the only herbicide that exceeded its EQS value at the sampling stations of Turhal. The concentrations of aclonifen were calculated as above only its MAC-EQS value with 173% and 183% exceedances at the Y-17 and Y-18 sampling stations, respectively. At both of the sampling stations, aclonifen herbicide was observed only in one measurement out of eight sampling periods corresponding to 12.5% detection frequency in each of the sampling stations. Since the concentrations of the aclonifen herbicide were determined as below its AA-EQS values at both of the sampling stations in Turhal, the herbicide-type pesticide pollution is not an issue of concern for the water quality on an annual basis in the district.

Table 3.34 Potential Sources and Detection Percentages of the Herbicides Observed at the Y-17 and Y-18 Sampling Stations of Turhal

Stations	**Herbicides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Herbicides**
		AA-EQS	**MAC-EQS**		
Y-17	Aclonifen	-	173	12.5	**Agricultural Source:** - Not Exist **Industrial Source:** - The wastewater discharges of the agriculture industry-wheat, sunflower, sugarbeet, forage plants and fruit processing
Y-18	Aclonifen	-	183	12.5	

Regarding the agricultural uses of the herbicides, the agricultural engineers of Turhal District Directorate of Agriculture and Forestry (2019) stated that the herbicide spraying practices for the agricultural lands of Turhal are taken place between the March and June periods. Whereas, the concentrations of the aclonifen herbicide at the Y-17 and Y-18 sampling stations of Turhal were observed as above its MAC-EQS value only in the October sampling period. The discrepancy between the herbicide spraying schedule of the crops raised in Turhal and the detection months of the aclonifen herbicide above the EQS value indicates that the aclonifen pollution observed at the Y-17 and Y-18 sampling stations of Turhal is not related to the agricultural land use in Turhal.

3.4.4.4.7.3 Determination of the Potential Sources of Fungicide Pollution at the Y-17 and Y-18 Sampling Stations of Turhal

The fungicide-type pesticide pollution was not observed at the Y-17 and Y-18 sampling stations of the Turhal District.

3.4.4.4.8 Erbaa District (Y-36 and Y-37 Sampling Stations)

The Erbaa District embodies the transition climate, which comprises the typical characteristics of both mild sea climate and continental climate. The transition climate enables the Erbaa District to incorporate a favorable environment for the farming of the various agricultural crops. Since the diversity of the agricultural crops raised in Erbaa is quite high, the crops like tobacco, hazelnut, rice plant and hash, which require specific climatic conditions, are also grown in Erbaa (OKA Erbaa District Report, 2018). The red-colored crops given in Table 3.35 represent the dominant crops of Erbaa, which encompass the wide variety of crop types. The areal shares of most of the dominant crops were determined as quite high at the basin scale. For instance, as it is presented in Table 3.35, it was calculated that the tobacco, melon and grape farmlands occupy 94%, 42% and 25% of the total tobacco, melon and grape areas, respectively, located in the 26 districts of the basin.

Table 3.35 The Calculated Percentage Shares of the Crop Areas in the Erbaa District

Agricultural Crop	**Area of Agricultural Land, decare (TurkStat, 2020)**	**Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Erbaa District, %**	**Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %**
Wheat	145458	**43**	**5.0**
Barley	31139	**9**	4.0
Hazelnut	28200	**8**	**5.8**
Tobacco	20500	**6**	**94.0**
Grape	18232	**5**	**24.8**
Sunflower	18200	**5**	4.8
Alfalfa	17500	**5**	**7.2**
Bean	10005	3	**17.3**
Pepper	7905	2	**26.7**
Melon	6300	2	**42.7**
Maize	6284	2	2.1
Tomato	6180	2	**8.7**
Onion	5320	2	4.7
Potato	4200	1	**9.6**
Walnut	1600	0.5	3.5
Chickpea	1500	0.4	0.9
Rice Plant	1000	0.3	**9.1**
Hash	958	0.3	**5.8**
Okra	850	0.3	**12.1**
Aubergine	840	0.2	**8.4**
Cabbage	680	0.2	**17.8**
Rye	411	0.1	**8.8**

Table 3.35 (cont'd)

Agricultural Crop	Area of Agricultural Land, decare (TurkStat, 2020)	Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Erbaa District, %	Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the 26 Districts of the Basin, %
Triticale	411	0.1	0.3
Peach	350	0.1	1.6
Sugarbeet	307	0.1	0.2
Other Crops	Negligibly Small Portion		

3.4.4.4.8.1 Determination of the Potential Sources of Insecticide Pollution at the Y-36 and Y-37 Sampling Stations of Erbaa

As given in Table 3.36, dichlorvos was determined as the only insecticide type whose concentration is above its EQS value at the sampling stations of Erbaa. According to the agricultural engineers of Erbaa District Directorate of Agriculture and Forestry (2019), the insecticide spraying activities of the crops raised in Erbaa typically begins in March and lasts till the middle of July. On the other hand, the concentration of dichlorvos insecticide exceeded its EQS values in August, October and January. Therefore, the relation between the insecticide spraying schedule of the agricultural lands in Erbaa and the EQS exceedance periods of the insecticides observed at the sampling stations of Erbaa was identified as substantially poor; therefore, the agricultural land use in Erbaa was not determined as the potential source to contribute to the insecticide pollution observed at the Y-36 and Y-37 sampling stations of Erbaa. When the industrial sources of the pesticide pollution within the boundaries of Erbaa are taken into account, it was seen that there is not existing the pesticide-related industry that discharges its wastewater in boundaries of Erbaa. In this respect, wastewater discharges from urban wastewater treatment plants, pesticide transport from the surrounding districts can be potential sources of the dichlorvos pollution observed at the Y-36 and Y-37 sampling stations.

Table 3.36 Potential Sources and Detection Percentages of the Insecticides Observed at the Y-36 and Y-37 Sampling Stations of Erbaa

Stations	**Insecticides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Insecticides**
		AA-EQS	**MAC-EQS**		
Y-36	Dichlorvos	1358	9650	12.5	**Agricultural Source:** - Not Exist **Industrial Source:** - Not Exist
Y-37	Dichlorvos	6317	31052	37.5	

3.4.4.4.8.2 Determination of the Potential Sources of Herbicide Pollution at the Y-36 and Y-37 Sampling Stations of Erbaa

As provided in Table 3.37, regarding the herbicide-type pesticides, the concentrations of ethalfluralin and bifenox were calculated as above their EQS values at the sampling stations of Erbaa. It was determined that while ethalfluralin exceeded only its MAC-EQS value with 218% and 326% at the Y-36 and Y-37 sampling stations, respectively, bifenox exceeded both of its AA-EQS and MAC-EQS values with 281% and 772%, respectively, only at the Y-37 sampling station.

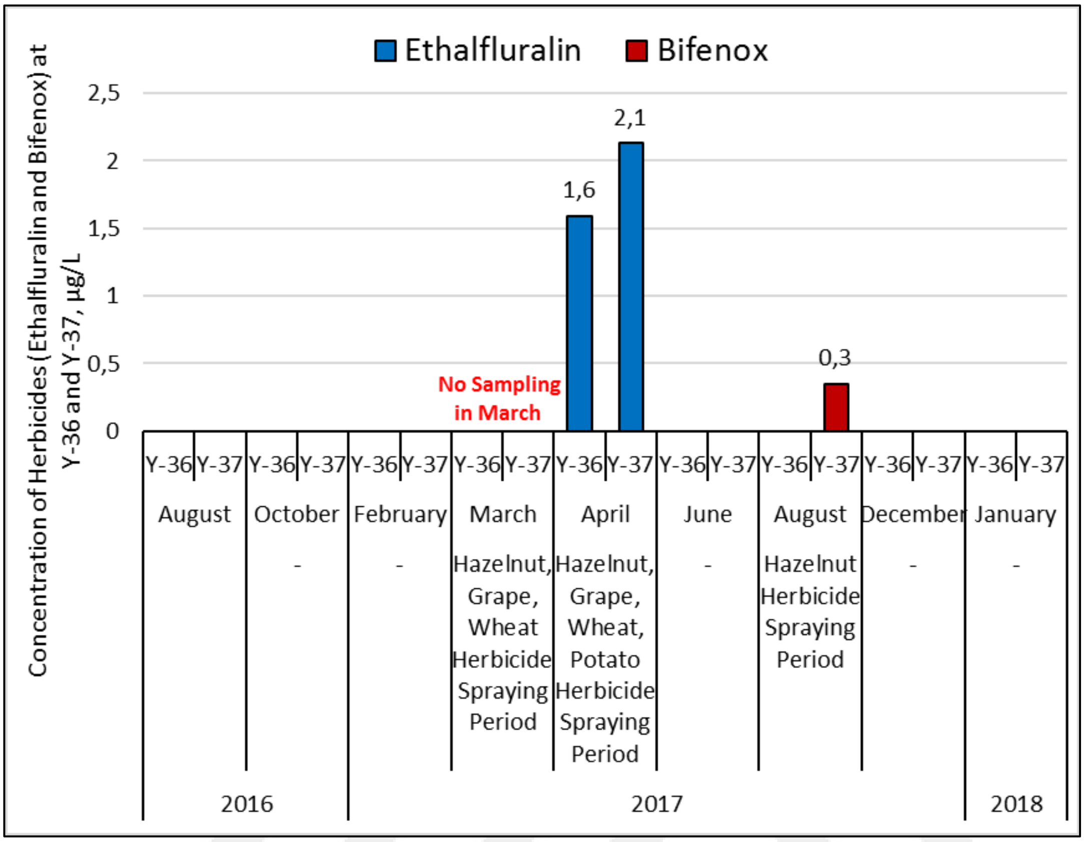

Figure 3.22 Correlation Between EQS Exceedance Months of Herbicides (at Y-36 and Y-37) and Herbicide Spraying Periods for the Dominant Crops of Erbaa

As it is depicted in Figure 3.22, the EQS exceedances of the ethalfluralin herbicide was observed only in the April sampling period. The agricultural engineers of Erbaa District Directorate of Agriculture and Forestry (2019) reported that April is the month of herbicide spraying activities for the wheat, hazelnut, grape and potato crops, which were all determined as the dominant crops of Erbaa. These crops have herbicide spraying activities also in the month of March. Based on the compatibility between the herbicide spraying periods of the wheat, hazelnut, grape and potato crops of Erbaa and the EQS exceedance periods of the ethalfluralin herbicide, 145458 da wheat, 28200 da hazelnut, 18232 da grape and 4200 da potato fields were identified as the potential sources of the ethalfluralin pollution observed at the Y-36 and Y-37 sampling stations of Erbaa. Regarding the bifenox detection at the Y-37 sampling station of Erbaa, as it is shown in Figure 3.22, the EQS exceedance of the bifenox herbicide was observed in the August sampling period. The agricultural engineers of Erbaa District Directorate of Agriculture and Forestry (2019) specified that the August period is responsible for the herbicide spraying activities of the hazelnut crop raised in Erbaa. In view of this temporal relation, it was determined that the 28200 da hazelnut farmlands located in Erbaa has the potential to contribute to the bifenox pollution observed at the Y-37 sampling station of Erbaa.

Table 3.37 Potential Sources and Detection Percentages of the Herbicides Observed at the Y-36 and Y-37 Sampling Stations of Erbaa

<table>
<tr><th rowspan="2">Stations</th><th rowspan="2">Herbicides</th><th colspan="2">EQS Exceedance %</th><th rowspan="2">Detection Frequency %</th><th rowspan="2">Potential Sources of the Observed Herbicides</th></tr>
<tr><th>AA-EQS</th><th>MAC-EQS</th></tr>
<tr><td>Y-36</td><td>Ethalfluralin</td><td>-</td><td>218</td><td>12.5</td><td rowspan="2">Agricultural Source:
- Wheat : 145458 da
- Hazelnut : 28200 da
- Grape: 18232 da
- Potato: 4200 da
Industrial Source:
- Not Exist</td></tr>
<tr><td rowspan="2">Y-37</td><td>Ethalfluralin</td><td>-</td><td>326</td><td>12.5</td></tr>
<tr><td>Bifenox</td><td>281</td><td>772</td><td>12.5</td><td>Agricultural Source:
- Hazelnut : 28200 da
Industrial Source:
- Not Exist</td></tr>
</table>

3.4.4.4.8.3 Determination of the Potential Sources of Fungicide Pollution at the Y-36 and Y-37 Sampling Stations of Erbaa

As it is provided in Table 3.38, in regard to the fungicide-type pesticide pollution, the HCB fungicide was observed at the sampling stations of Erbaa. The concentration of HCB fungicide was calculated as above its MAC-EQS value with

547% exceedance in one measurement out of eight sampling periods at the Y-36 sampling station.

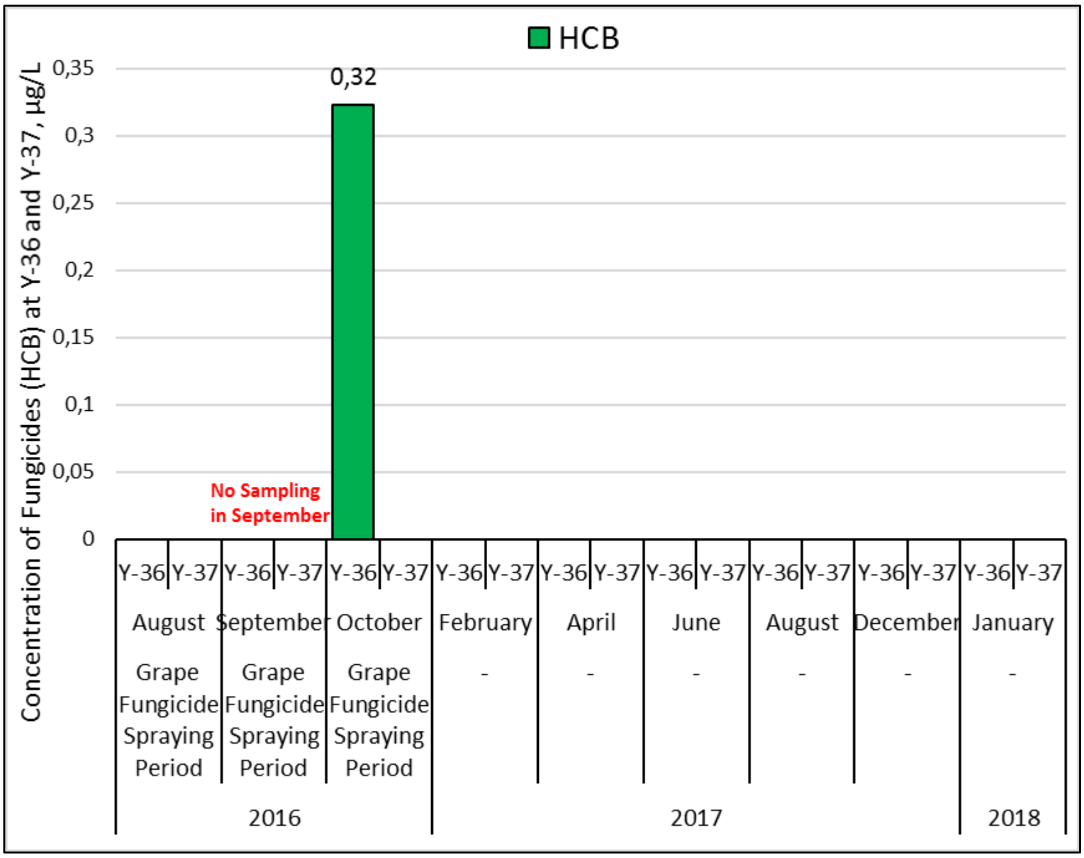

Figure 3.23 Correlation Between EQS Exceedance Months of Fungicides (at Y-36 and Y-37) and Fungicide Spraying Periods for the Dominant Crops of Erbaa

As it can be seen in Figure 3.23, the EQS exceedance of the HCB fungicide was observed only in October. When the fungicide spraying schedules of the agricultural crops of Erbaa, which are provided by the agricultural engineers of Erbaa District Directorate of Agriculture and Forestry (2019), were examined, the grape crop was determined as the only dominant crop that is sprayed by the fungicides in the months of August, September and October. As it is introduced in the database of Meteoblue Climate History of Erbaa (2019), the monthly average precipitation amounts of Erbaa in the months of August, September and October are 9 mm, 22 mm, 52 mm, respectively. This dramatic upward trend of the precipitation in Erbaa indicates that the pesticide wash in the farmlands of the district is most likely to occur in October rather than August and September. In this respect, it was figured out that the observations of the EQS exceedance of the HCB fungicide only in October was an expected outcome of the fungicide spraying activities of the grape crop. By taking into consideration all these compatibility factors, it was determined that the HCB pollution observed at the Y-36 sampling station has the high potential to be originated from the 18200 da grape area of Erbaa, which was determined as being responsible for 25% of the total grape lands located within the 26 districts of the basin.

Table 3.38 Potential Sources and Detection Percentages of the Fungicides Observed at the Y-36 and Y-37 Sampling Stations of Erbaa

Stations	**Fungicides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Fungicides**
		AA-EQS	**MAC-EQS**		
Y-36	HCB	-	547	12.5	**Agricultural Source:** - Grape: 18200 da **Industrial Source:** - Not Exist
Y-37	-	-	-	-	-

3.4.4.5 Amasya Province

The Amasya Province embodies the largest agricultural land compared to the other provinces of the basin. In total, 11 water quality sampling stations exist within the boundaries of Amasya. The water quality measurement stations are located in the five districts of Amasya, which comprise the Merkez, Göynücek, Merzifon, Suluova and Taşova districts. Among these districts, the highest altitude belongs to the

Merzifon district with 746 m. The altitudes of the districts of Amasya are quite similar; consequently, there is no sharp difference between the climatic conditions of the districts of Amasya. Correspondingly, the types, amounts and occurrence periods of the pests that attack on the same type of crops show similar profiles in all districts of Amasya. Different from the provinces mentioned so far, the districts of the Amasya Province embody the same agricultural spraying schedules for the same crop types because the geographical and climatic characteristics of the districts of Amasya are quite the same. Similar geography and climatic conditions create similar habitats for the growth of insects, weeds and fungal diseases (Personal Communication with the Agricultural Engineers of Amasya Provincial Directorate of Agriculture and Forestry, 2019). The agricultural engineers of Amasya Provincial Directorate of Agriculture and Forestry (2019) specify that since there is no significant change in the geographical and climatic characteristics from district to district in Amasya, the agricultural spraying schedules are typically the same for the districts of Amasya without district-specific differences. Therefore, in the case of the Amasya Province, the agrochemical spraying assessments were not divided into sub-regions, instead, it was treated as a whole. In the following sections, the agricultural profile of the Amasya Province will be assessed, and the temporal correlation between the pesticide spraying schedules of each dominant crop raised in the province and the pesticide occurrence periods at the sampling stations of the province will be analyzed and discussed in detail.

Table 3.39 The Calculated Percentage Shares of the Crop Areas in the Amasya Province

Agricultural Crop	Area of Agricultural Land, decare (TurkStat, 2020)	Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Amasya Province, %	Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the Eight Provinces of the Basin, %
Wheat	917727	**54**	**31**
Barley	219296	**13**	**28**
Sunflower	127692	**8**	**34**
Maize	118674	**7**	**40**
Sugarbeet	71857	4	**42**
Onion	48360	3	**42**
Sweet Cherry	25460	1	**66**
Alfalfa	21313	1	**9**
Chickpea	15615	1	**10**
Hash	14338	1	**87**
Apple	13069	1	**47**
Tomato	12229	1	**17**
Walnut	11410	1	**25**
Oat	8371	0.5	**48**
Bean	8310	0.5	**11**
Cucumber	8195	0.5	**51**
Grape	7633	0.4	**10**
Potato	6460	0.4	**15**
Triticale	6030	0.4	4
Peach	5985	0.4	**27**
Okra	5760	0.3	**82**
Lettuce	4520	0.3	**35**
Aubergine	2990	0.2	**30**
Pepper	2373	0.1	**8**

Table 3.39 (cont'd)

Agricultural Crop	Area of Agricultural Land, decare (TurkStat, 2020)	Percentage Share of the Crop Area Among the Areas of the Other Type of Crops Raised in the Amasya Province, %	Percentage Share of the Crop Area Among the Areas of Same Crop Types Raised in the Eight Provinces of the Basin, %
Spinach	2350	0.1	**27**
Pea	1370	0.1	**53**
Lentil	1282	0.1	**5**
Pear	1254	0.1	**26**
Rice	1238	0.1	**11**
Watermelon	1005	0.1	**7**
Sour Cherry	870	0.1	**16**
Sainfoin	845	0.05	2
Leek	790	0.05	**22**
Melon	770	0.05	**8**
Tobacco	770	0.05	4
Rye	692	0.04	**15**
Garlic	524	0.03	**5**
Hazelnut	250	0.01	0.1
Cabbage	205	0.01	**5**
Soybean	135	0.01	4
Other Crops	Negligibly Small Portion		

As it is presented in Table 3.39, the agricultural land use in the five districts of the Amasya Province encompasses the farming of the various types of agricultural crops with significantly high areal shares. The red-colored crops given in Table 3.39 represent the dominant crops, which have areal shares above 5% at the basin scale or/and at the province scale. Since the areal shares of the crops raised in Amasya were calculated as considerably high, the number of the dominant crops was also determined as quite high. In total, the 35 crops were determined as the dominant crops of Amasya. In the following sections, the potential sources of the pesticides observed at the sampling stations of Amasya will be identified among these pre-selected 35 dominant crops.

3.4.4.5.1 Determination of the Potential Sources of Insecticide Pollution at the Sampling Stations of the Amasya Province

As it is provided in Table 3.40, regarding the insecticide-type pesticide pollution, the concentrations of dichlorvos, diflubenzuron, prothiofos, HCH and fenthion were calculated as above their EQS values at the sampling stations of Amasya. Among these insecticides, dichlorvos was observed at all of the 11 sampling stations of Amasya. After dichlorvos, diflubenzuron was determined as the second most observed insecticide at the sampling stations of Amasya. Diflubenzuron is followed by the HCH, fenthion, and prothiofos insecticides. As it is shown in Figure 3.24, the concentrations of these insecticides were calculated as above their EQS values in the August and October sampling periods. Almost all EQS exceedances of dichlorvos were observed in August. On the other hand, the concentrations of all diflubenzuron, prothiofos, HCH, and fenthion insecticides were observed as above their EQS values in October. The agricultural engineers of Amasya Provincial Directorate of Agriculture and Forestry (2019) reported that August is the month of insecticide spraying activities for the tomato, apple, and pear crops. The insecticide spraying activities of apple continue till the end of September. The agricultural engineers of Amasya Provincial Directorate of Agriculture and Forestry (2019) stated that, in the month of October, the insecticide spraying activities are not applied for any crops raised in the province. On the other hand, it was determined that October is the month of EQS exceedance for all of the dichlorvos, diflubenzuron, prothiofos, HCH and fenthion insecticides. Despite the absence of the insecticide spraying activities in October, all five type of insecticides were observed in October. This discrepancy indicates that there exist driving forces that trigger release of these insecticides in October more severely than in August and September. Precipitation is one of the major driving forces that have considerable influence on the wash and spread of the pesticides from their application area to the non-target sites. When the monthly precipitation trend of Amasya was taken into account, it was revealed that the monthly average precipitation amounts in Amasya are 10 mm, 20 mm and 35 mm in August, September and October, respectively (Turkish State Meteorological Service , 2020). The precipitation trend of Amasya shows that the precipitation amounts in Amasya from August to October are tripled by following a drastic upward trend. Therefore, most of the insecticides applied in August were expected to emerge in the river in the following months like September and October, with the impact of dramatically increasing precipitation events. As it was expected, the elevated concentrations of the five different insecticides in October strongly point out the insecticide spraying activities of apple, tomato and pear crops performed in the months of August and September. As a result of all these analysis and assessments, 13069 da apple, 12229 da tomato and 1254 da pear fields were identified as the potential sources of dichlorvos, diflubenzuron, HCH, prothiofos, and fenthion pollution observed at the sampling stations of Amasya.

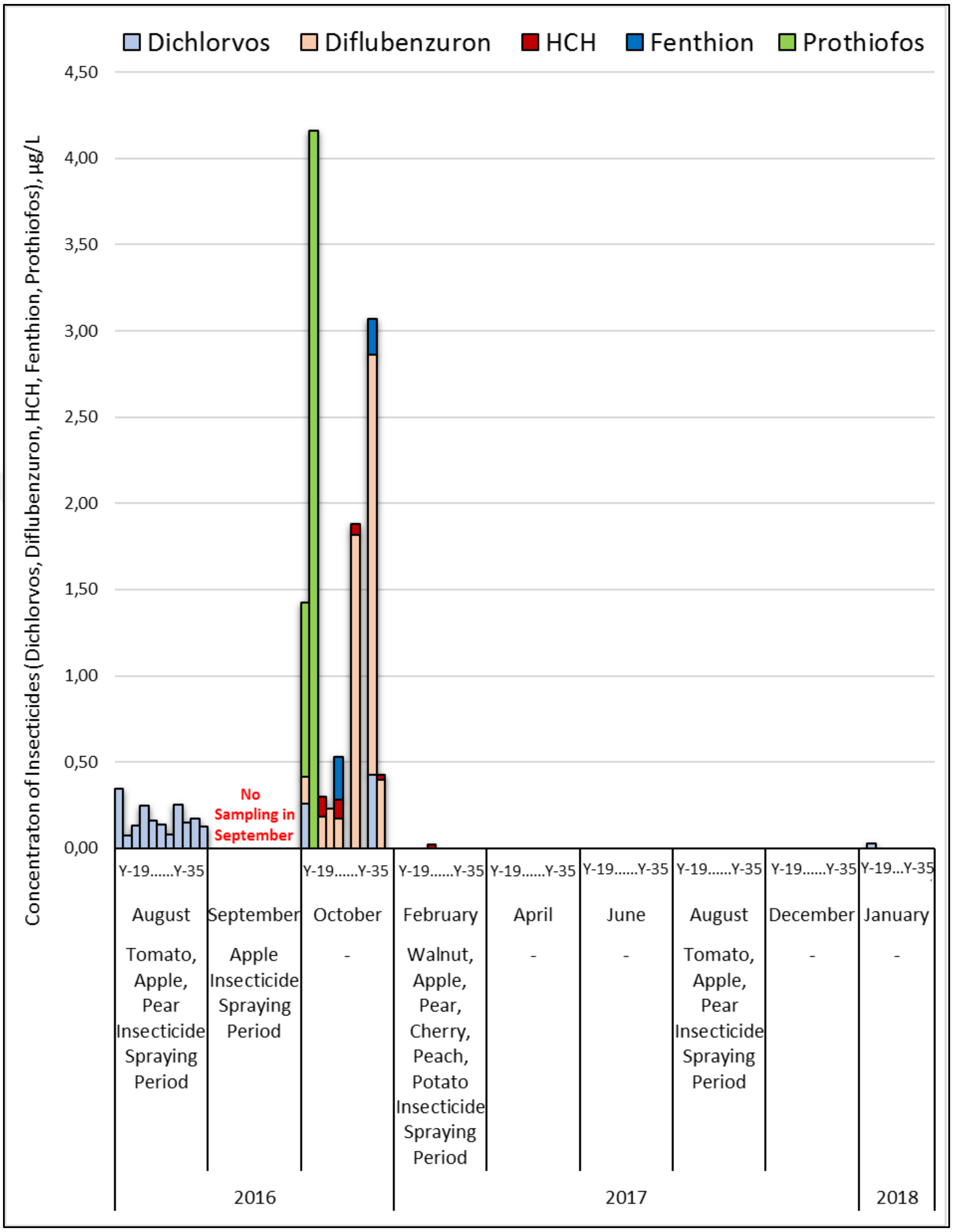

Figure 3.24 Correlation Between EQS Exceedance Months of Insecticides at the 11 Sampling Stations and Insecticide Spraying Periods for the Dominant Crops of Amasya

Table 3.40 Potential Sources and Detection Percentages of the Insecticides Observed at the Sampling Stations of the Amasya Province

Stations	Insecticides	EQS Exceedance %		Detection Frequency %	Potential Sources of the Observed Insecticides
		AA-EQS	MAC-EQS		
Y-19	Dichlorvos	12481	48958	25.0	**Agricultural Sources:** - Apple Farmlands: 13069 da - Tomato Farmlands: 12229 da - Pear Farmlands: 1254 da **Industrial Sources:** - The Wastewater Discharges of the Broad Range of Flour Production, Agricultural Products, Vegetable and Fruit Processing Facilities located in Amasya
	Diflubenzuron	-	19	12.5	
	Prothiofos	49	-	12.5	
Y-20	Dichlorvos	2052	10630	25.0	
	Prothiofos	449	-	12.5	
Y-21	HCH	-	200	12.5	
	Dichlorvos	2698	18833	12.5	
	Diflubenzuron	-	39	12.5	
Y-22	Dichlorvos	5057	35012	12.5	
	Diflubenzuron	-	78	12.5	
Y-33	HCH	-	168	25.0	
	Dichlorvos	3326	23144	12.5	
	Fenthion	7	-	12.5	
	Diflubenzuron	-	32	12.5	
Y-23	Dichlorvos	2780	19396	12.5	
Y-24	Dichlorvos	1866	11481	14.0	
	HCH	-	68	14.0	
	Diflubenzuron	116	1296	14.0	
Y-31	Dichlorvos	5182	35871	12.5	
Y-32	Dichlorvos	13705	60909	28.6	
	Fenthion	2	-	14.3	
	Diflubenzuron	184	1771	14.3	
Y-34	HCH	-	-	14.0	
	Dichlorvos	3970	24107	14.0	
	Diflubenzuron	-	205	14.0	
Y-35	Dichlorvos	2571	17963	12.5	

3.4.4.5.2 Determination of the Potential Sources of Herbicide Pollution at the Sampling Stations of the Amasya Province

As it is given in Table 3.41, bifenox, ethalfluralin and diflufenican were observed as herbicide-type pesticides at the sampling stations of Amasya. While the concentrations of bifenox were calculated as above both of its AA-EQS and MAC-EQS values, the concentrations of ethalfluralin and diflufenican were determined as above only their MAC-EQS values. Among these three herbicides, bifenox was determined as the most widely spread herbicide across the Amasya. Bifenox was observed at the five different sampling stations out of 11 sampling stations of Amasya, whereas ethalfluralin and diflufenican were observed at the four and two of these sampling stations, respectively.

As it can be seen in Figure 3.25, the EQS exceedances of the bifenox herbicide was observed only in the August sampling period. According to the agricultural engineers of Amasya Provincial Directorate of Agriculture and Forestry (2019), August is the month of herbicide spraying activities for the rice crop cultivated in Amasya. In this regard, 1238 da rice fields were determined as the potential source of the bifenox pollution observed at the sampling stations of Amasya. Regarding the ethalfluralin and diflufenican pollution, ethalfluralin and diflufenican herbicides were both observed only in the April sampling period. The agricultural engineers of the Amasya Provincial Directorate of Agriculture and Forestry (2019) stated that wheat, onion and sunflower crops are sprayed by the herbicides in the month of April. By taking into account these temporally compatible relations, 917727 da wheat, 127692 da sunflower, and 48360 da onion fields were identified as the potential sources of the ethalfluralin and diflufenican pollution observed at the sampling stations of Amasya.

Table 3.41 Potential Sources and Detection Percentages of the Herbicides Observed at the Sampling Stations of the Amasya Province

Stations	**Herbicides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Herbicides**
		AA-EQS	**MAC-EQS**		
Y-20	Bifenox	34	177	12.5	- Rice Farmlands: 1238 da
Y-22	Bifenox	70	263	12.5	
Y-32	Bifenox	185	461	14.3	
Y-33	Bifenox	156	470	12.5	
Y-23	Bifenox	124	393	12.5	
Y-33	Ethalfluralin		30	12.5	- Wheat Farmlands: 917727 da - Sunflower Farmlands: 127692 da - Onion Farmlands: 48360 da
Y-23	Ethalfluralin	-	23	12.5	
Y-34	Diflufenican	-	77	14.0	
	Ethalfluralin	-	20	14.0	
Y-35	Diflufenican	-	155	12.5	
	Ethalfluralin	-	36	12.5	

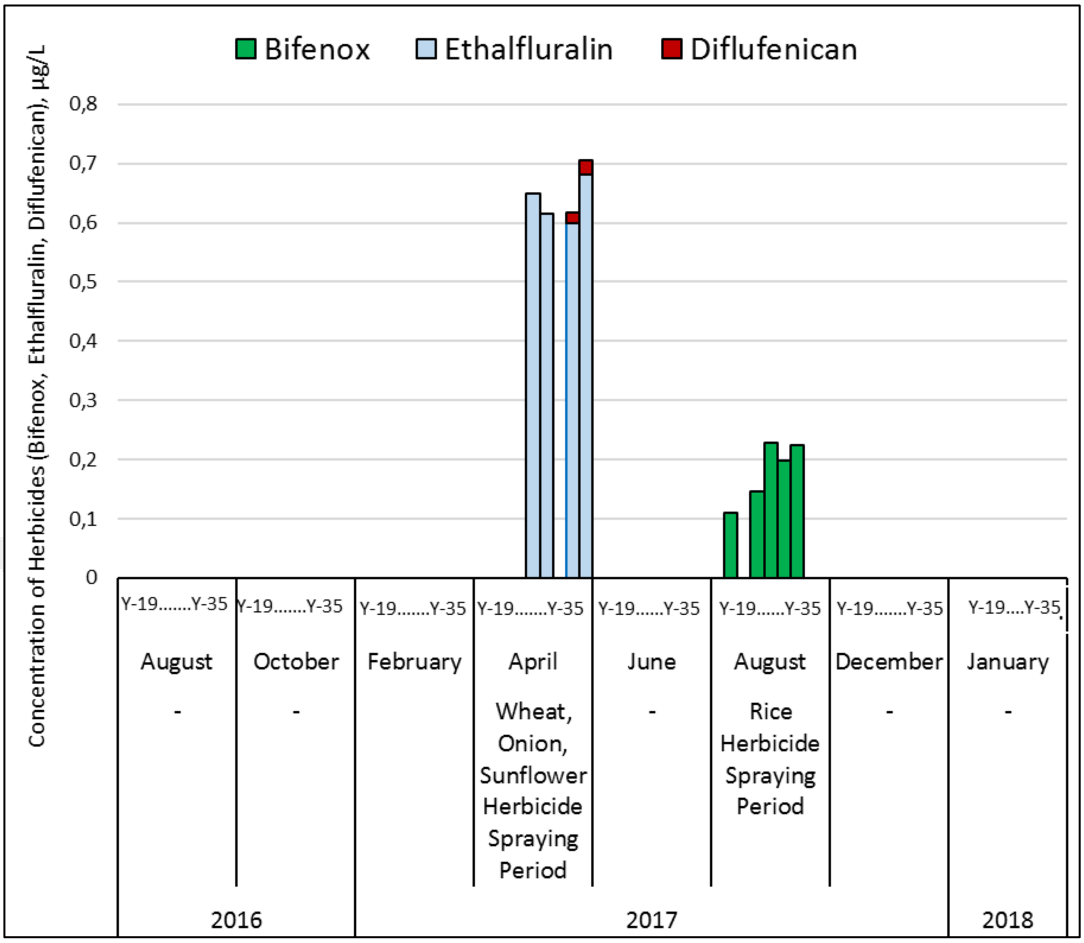

Figure 3.25 Correlation Between EQS Exceedance Months of Herbicides at the 11 Sampling Stations and Herbicide Spraying Periods for the Dominant Crops of Amasya

3.4.4.5.3 Determination of the Potential Sources of Fungicide Pollution at the Sampling Stations of the Amasya Province

As it is presented in Table 3.42, HCB and fenpropimorph were observed as the fungicide-type pesticides at the sampling stations of Amasya. The concentrations of HCB were calculated as above its EQS values at two of the 11 sampling stations, whereas the concentrations of fenpropimorph were calculated as above its EQS values only at one sampling station out of 11 sampling stations located in Amasya.

As it is depicted in Figure 3.26, the EQS exceedances of HCB were observed in the August and October sampling periods. On the other hand, the concentrations of fenpropimorph were determined as above its EQS value only in April. When the fungicide spraying schedules of the crops raised in Amasya were examined, it was revealed that August is the month of fungicide spraying for cucumber, aubergine, and onion crops of Amasya. The wheat crop has a fungicide spraying schedule applied in October. The walnut, tomato, pear, apple, and cherry crops have fungicide spraying schedules applied in April (Personal Communication with the Agricultural Engineers of Amasya Provincial Directorate of Agriculture and Forestry, 2019). In the light of the correlations provided in Figure 3.26, 26330 da cherry, 13069 da apple, 12229 da tomato, 11410 da walnut, and 1254 da pear fields were identified as the potential sources of the fenpropimorph pollution observed at the Y-32 sampling station of Amasya. Furthermore, 917727 da wheat, 48360 da onion, 8195 da cucumber and 2990 da aubergine farmlands were determined as the potential sources of HCH pollution observed at the Y-19 and Y-33 sampling stations of Amasya.

Table 3.42 Potential Sources and Detection Percentages of the Fungicides Observed at the Sampling Stations of the Amasya Province

Stations	Fungicides	EQS Exceedance %		Detection Frequency %	Potential Sources of the Observed Fungicides
		AA-EQS	MAC-EQS		
Y-19	HCB	-	2658	25.0	- Wheat Farmlands: 917727 da - Onion Farmlands: 48360 da - Cucumber Farmlands: 8195 da - Aubergine Farmlands: 2990 da
Y-33	HCB		59	25.0	
Y-32	Fenpropimorph	47	-	14.3	- Cherry Farmlands: 26330 da - Apple Farmlands: 13069 da - Tomato Farmlands: 12229 da - Walnut Farmlands: 11410 da - Pear Farmlands: 1254 da

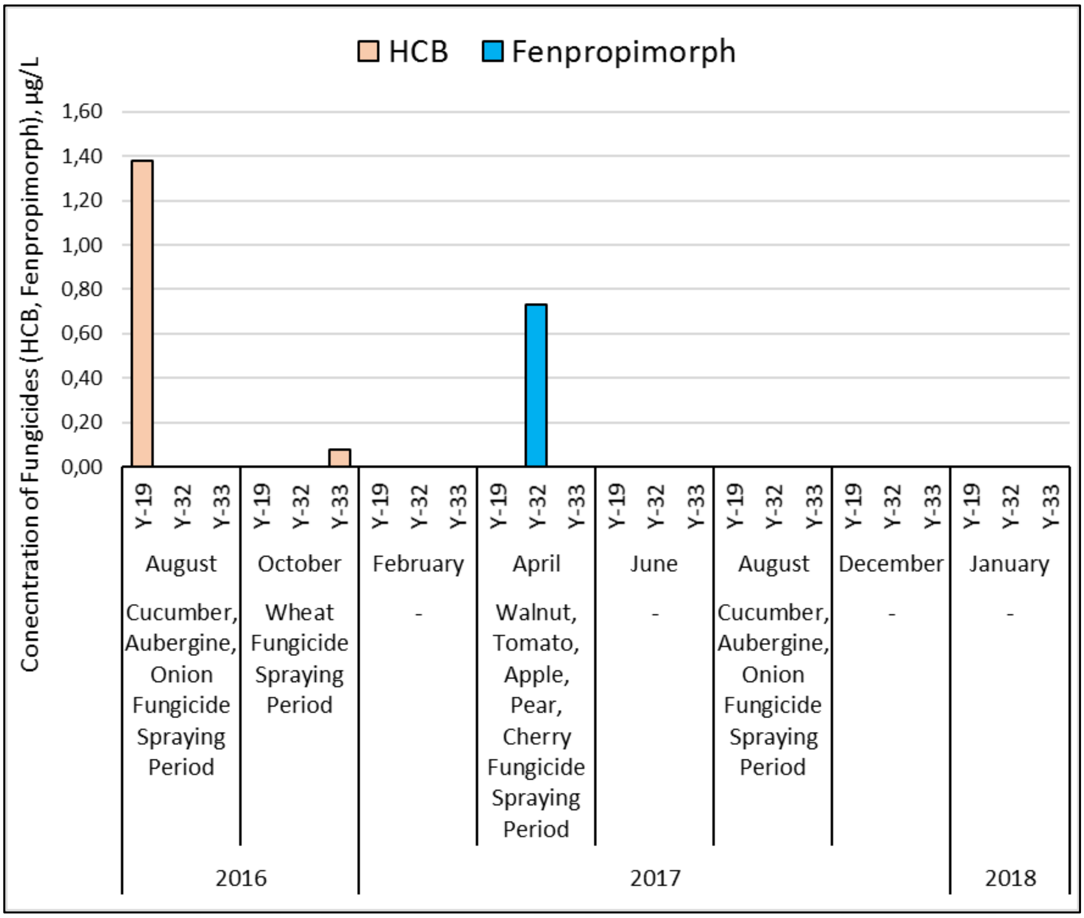

Figure 3.26 Correlation Between EQS Exceedance Months of Fungicides at the 11 Sampling Stations and Fungicide Spraying Periods for the Dominant Crops of Amasya

3.4.5 Spatiotemporal Distribution and Source Identification of Pesticides

Agriculture is a constantly growing field to serve and meet the drastically rising need of the global food sector. This dramatic increase in agricultural production brings about the vast majority of concerns associated with agricultural practices. One of the major constraints encountered in farming activities is the occurrence of pests that attack and deteriorate the farmlands. The existence of these invaders in the agricultural fields creates a need for the crop protection and promoting of crop yield by the plant protection products, in other words, today's great deal of concern: pesticides. Pesticides are one of the most widely used micropollutant group with their broad range of applications in different fields of daily life. Most of the pesticides have persistent, bioaccumulative, and toxic properties, which correspond to the long-term existence in the natural environment, the accumulation in the ecologic cycle, and the high risk to living organisms, respectively. Since pesticides can reach to river bodies via various mechanisms like spray drift, surface runoff, erosion and atmospheric deposition, river bodies are one of the most vulnerable environmental compartment to pesticide pollution. Consequently, the pesticide pollution in the river bodies has gained great interest as an urgent environmental issue all over the world. This thesis has focused on the target-specific source identification of the pesticide pollution in the Yeşilırmak River Basin. In order to fulfill the target-specific approach, the district-specific agricultural characterization, pollution analysis and source identification were performed at the corresponding water quality sampling stations in the boundaries of the individual districts of the basin.

The existence of the pests in a particular region considerably depends on the climatic, geographic and topographic characteristics of the target site. The same crop type raised in the different territories can be exposed to the different kinds and amounts of insects, weeds and fungal diseases. Thus, the location of agricultural fields has critical importance for the determination of the type, dosage and environmental fate of the pesticides applied on the agricultural lands. In this respect, the district-specific analysis conducted within the scope of this thesis is thought to play a key role for the reliable and precise source identification because the type and amount of the insecticides, herbicides and fungicides sprayed on the agricultural lands are primarily dependent on the type of the crop raised in the individual agricultural fields and the implementation strategies of the localized agricultural practices, which are characterized by the district-specific climate, geography and topography. Within the scope of the district-specific source identification, the dominant crops in terms of their potential to contribute to the pesticide pollution were determined for each of the districts of the basin. The quite comprehensive and elaborative data collection and compilation regarding the agricultural land use profiles and the pesticide spraying schedules specific to each crop type raised in each district were carried out by personally contacting with the agricultural engineers of the Provincial and District Directorates of Agriculture and Forestry. As a result of these personal interviews, detailed inventories on the district-specific agricultural characteristics and practices were prepared for each of the districts that locate the sampling stations in their boundaries. In the light of these inventories, the temporal relation between the EQS exceedance months of the pesticides observed at the sampling stations of each district and the pesticide usage schedules of the dominant crops raised in the corresponding districts were analyzed and assessed by taking into account the impact of the district-specific monthly average precipitation amounts on the temporal trend of the pesticide occurrences. In this respect, the potential agricultural sources of pesticides observed at the sampling stations of each district were identified by adressing district-specific analysis and assessments. The overall results of the district-specific agricultural source identification of pesticides in the river basin are summarized in Table 3.43.

Table 3.43 Agricultural Sources of the Pesticides in Each District of the Yeşilırmak River Basin

District - Province	**Pesticide Types**	**Pesticides**	**Potential Agricultural Sources of the Observed Pesticides**
Köse - Gümüşhane	Insecticides	Dichlorvos	- Not Exist
		Diflubenzuron	
		Permethrin	
		4,4'-DDD	
	Herbicides	Diflufenican	- Wheat Farmland: 34509 da
Kelkit - Gümüşhane	Insecticides	Dichlorvos	- Bean Farmland: 4400 da - Potato Farmland: 3500 da
	Herbicides	Bifenox	- Maize Farmland: 8000 da
Çamoluk - Giresun	Insecticides	Dichlorvos	- Not Exist
		Fenpropathrin	- Not Exist
	Herbicides	Aclonifen	- Not Exist
Şebinkarahisar - Giresun	Insecticides	Diflubenzuron	- Wheat Farmland: 83612 da
		HCH	
		Dichlorvos	- Not Exist
	Herbicide	Aclonifen	- Not Exist
Koyulhisar - Sivas	Insecticide	Dichlorvos	- Not Exist
	Herbicide	Bifenox	
		Ethalfluralin	

Table 3.43 (cont'd)

District - Province	Pesticide Types	Pesticides	Potential Agricultural Sources of the Observed Pesticides
Zara - Sivas	Insecticide	Diflubenzuron	-Wheat Farmland: 132887 da
		HCH	
		Fenthion	
		Dichlorvos	- Not Exist
	Herbicide	Ethalfluralin	-Wheat Farmland: 132887 da
Reşadiye - Tokat	Insecticide	Dichlorvos	- Cherry Farmland: 445 da - Cabbage Farmland: 380 da
		Fenthion	
	Fungicide	Fenpropimorph	- Walnut Farmland: 3664 da - Cherry Farmland: 445 da
Niksar - Tokat	Insecticide	Dichlorvos	- Alfalfa Farmland: 12500 da - Bean Farmland: 8116 da - Walnut Farmland: 6000 da
	Herbicide	Aclonifen	- Cabbage Farmland: 460 da
		Ethalfluralin	- Potato Farmland: 8500 da - Grape Farmland: 6854 da - Melon Farmland: 4200 da
Merkez - Tokat	Herbicide	Aclonifen	- Chickpea Farmland: 30000 da - Sugarbeet Farmland: 25583 da - Onion Farmland: 9240 da - Garlic Farmland: 8000 da - Grape Framland : 22561 da - Peach, Cherry, Apple Trees
		Ethalfluralin	- Barley Farmland: 80972 da - Wheat Farmland: 67373 da
Almus - Tokat	Insecticide	Diflubenzuron	- Not Exist
		Dichlorvos	
	Fungicide	HCB	
Pazar - Tokat	Insecticide	Diflubenzuron	- Tomato Farmland: 14920 da - Sugarbeet Farmland : 9210 da - Bean Farmland: 3600 da - Melon Farmland: 1600 da
	Herbicide	Ethalfluralin	-Wheat Farmland: 19069 da
		Aclonifen	- Not Exist

Table 3.43 (cont'd)

District - Province	Pesticide Types	Pesticides	Potential Agricultural Sources of the Observed Pesticides
Sulusaray - Tokat	Insecticide	Dichlorvos	- Not Exist
	Herbicide	Aclonifen	
	Fungicide	HCB	
Turhal - Tokat	Insecticide	Diflubenzuron	- Tomato Farmland: 19233 da - Melon Farmland : 4000 da - Pepper Farmland: 3800 da - Aubergine Farmland: 1500 da
		Dichlorvos	
		HCH	
		Prothiofos	
	Herbicide	Aclonifen	- Not Exist
Erbaa - Tokat	Insecticide	Dichlorvos	- Not Exist
	Herbicide	Ethalfluralin	- Wheat Farmland : 145458 da - Hazelnut Farmland :28200 da - Grape Farmland: 18232 da - Potato Farmland: 4200 da
		Bifenox	- Hazelnut Farmland : 28200 da
	Fungicide	HCB	- Grape Farmland: 18200 da
Amasya (All Districts)	Insecticide	Dichlorvos	-Apple Farmland: 13069 da -Tomato Farmland: 12229 da - Pear Farmland: 1254 da
		Diflubenzuron	
		HCH	
		Fenthion	
		Prothiofos	
	Herbicide	Bifenox	- Rice Farmlands: 1238 da
		Ethalfluralin	- Wheat Farmland: 917727 da - Sunflower Farmland: 127692 da - Onion Farmland: 48360 da
		Diflufenican	
	Fungicide	HCB	- Wheat Farmland: 917727 da - Onion Farmland: 48360 da - Cucumber Farmland: 8195 da - Aubergine Farmland: 2990 da
		Fenpropimorph	- Cherry Farmland: 26330 da - Apple Farmland: 13069 da - Tomato Farmland: 12229 da - Walnut Farmland: 11410 da - Pear Farmland: 1254 da

Table 3.43 (cont'd)

District - Province	Pesticide Types	Pesticides	Potential Agricultural Sources of the Observed Pesticides
Ladik - Samsun	Insecticide	Dichlorvos	- Sunflower Farmland:12940 da
	Herbicide	Aclonifen	- Bean Farmland: 6750 da
		Bifenox	
		Ethalfluralin	- Wheat Farmland: 80188 da - Sunflower Farmland:12940 da
İlkadım - Samsun	Insecticide	Dichlorvos	- Hazelnut Farmland: 5300 da
		Diflubenzuron	
	Herbicide	Aclonifen	- Not Exist
		Ethalfluralin	- Wheat Farmland: 22379 da
	Fungicide	HCB	- Bean Farmland: 1400 da - Hazelnut Farmland: 5300 da
Çarşamba - Samsun	Insecticide	Dichlorvos	- Hazelnut Farmland:455500 da - Pepper Farmland: 8676 da - Bean Farmland: 4080 da - Lettuce Farmland: 1970 da - Kiwi Farmland: 2500 da
		Diflubenzuron	
		HCH	
	Herbicide	Bifenox	- Hazelnut Farmland:455500 da - Maize Farmland: 47952 da - Rice Farmland: 7849 da - Peach Farmland: 6000 da
		Ethalfluralin	-Wheat Farmland: 6394 da
	Fungicide	HCB	- Hazelnut Farmland:455500 da - Pepper Farmland: 8676 da - Bean Farmland: 4080 - Lettuce Farmland: 1970 da
Merkez - Çorum	Insecticide	Dichlorvos	- Grape Farmland: 7558 da - Apple Farmland: 1745 da - Tomato Farmland: 3821 da - Potato Farmland: 8000 da - Cucumber Farmland: 1236 da
		Diflubenzuron	
		HCH	
		Imidacloprid	
		Chlorfenapyr	
	Herbicide	Aclonifen	-Tomato Farmland: 3821 da - Cucumber Farmland: 1236 da
		Diflufenican	- Rice Farmland: 930 da - Tomato Farmland: 3821 da - Potato Farmland: 8000 da - Cucumber Farmland: 1236 da
	Fungicide	Fenpropimorph	- Sunflower Farmland: 104994 - Chickpea Farmland: 20000 - Grape Farmland: 7558 - Apple Farmland: 1745 - Lentil Farmland: 3105

Table 3.43 (cont'd)

District - Province	**Pesticide Types**	**Pesticides**	**Potential Agricultural Sources of the Observed Pesticides**
Alaca - Çorum	Insecticide	Dichlorvos	- Sugarbeet Farmland:15299 da - Onion Farmland: 12813 da
Saraykent - Yozgat	Insecticide	Dichlorvos	- Sugarbeet Farmland: 512 da
		Diflubenzuron	
	Herbicide	Ethalfluralin	- Chickpea Farmland : 3000 da - Lentil Farmland: 1703 da - Wheat Farmland: 57956 da
		Bifenox	- Sugarbeet Farmland: 512 da
	Fungicide	Fenpropimorph	- Grape Farmland: 867 da
Aydıncık - Yozgat	Insecticide	Dichlorvos	- Not Exist
		HCH	- Not Exist
	Herbicide	Aclonifen	- Not Exist
		Bifenox	- Sugarbeet Farmland: 2661 da

In addition to the district-specific source identification of the pesticide pollution, the relation between the spatial distribution of the agricultural areas across the basin and the basin-wide occurrence pathway of the 16 pesticides was determined and evaluated to identify the basin-wide contribution potential of the agricultural pressures to the pesticide pollution compared to the other sources of the pesticide pollution in the basin. In other words, the aim of this evaluation was, before focusing on the agricultural sources of the pesticides in detail, to clarify whether the impact of the agricultural land use on the pesticide pollution compared to the other sources of the pesticides is predominant or not. Another factor that has a considerable impact on the pesticide spread across the basin is the basin-wide intensity of the precipitation. Hence, this thesis has also paid particular attention to the analysis of the impact of monthly average precipitation amount on the number of pesticide detections at the corresponding sampling months all across the basin. Within the scope of this thesis, the altitude characteristics of the districts were also taken into account since the type of insects, weeds and fungal diseases exist in the districts substantially depend on the altitudinal changes of the districts. In this regard, the relation between the altitudes of the districts and the diversity of the pesticide types detected in the corresponding districts was also examined in order to identify the role of the altitudinal changes on the variability of the pesticide types that occur in the river. Another crucial factor that influences the occurrence of pesticides in the river is the environmental persistence of the pesticides observed in the river. In this context, the impact of soil and water half-lives of the 16 pesticides on their detection frequencies across the basin was analyzed as part of the assessment of the pesticide pollution in the river. Furthermore, the relation between the soil sorption capacities (a measure of mobility) of the 16 pesticides and their spatial distribution throughout the basin was also analyzed and evaluated within the context of this thesis.

Regarding the implementation of agricultural activities, the misuse and overuse of pesticides, the inadequate technical knowledge of farmers, the versatility of pesticide types applied on the agricultural crops, and the selection of pesticide spraying techniques that entail the drift and spread of pesticides are major problems that are required to be managed at the source. This study provides a better understanding of the development of functional solutions to overcome the site-specific agricultural problems by facilitating the simultaneous benefit of farmers, the environment, and the public. Furthermore, this study introduces a basis and profound strategy for the establishment of effective remediation techniques, the setting of target-oriented usage limits by regulations, and the development of sustainable agricultural practices. For the functional fulfillment of these goals, this study also offers the well-grounded and source-oriented implementation pathway, which favor the balance among the technical availability, economic viability, and well-improved ecologic life and water quality.

3.5 Conclusion and Recommendations

In this thesis, the spatial and temporal occurrence trends of the pesticide pollution across the Yeşilırmak River Basin were determined and, the agricultural sources of the pesticide pollution in the river basin were identified by addressing the district-specific analysis and assessment approach. In this respect, the following conclusions were drawn:

- Within the context of the assessment of the spatial distribution of the pesticides, the distribution of the agricultural areas across the river basin was determined as strongly compatible with the dissemination of the pesticides that exceeded their EQS values across the river basin. In this regard, it was seen that agricultural land use within the river basin prevails as being major pressure that determines the distribution pattern of the observed pesticide pollution across the river basin.
- Dichlorvos, which exceeded its EQS values at 39 sampling stations out of 42, was determined as the most widely dispersed pesticide across the river basin. Dichlorvos is followed by diflubenzuron, ethalfluralin and aclonifen, which were observed at 20 sampling stations, 16 sampling stations, and 14 sampling stations, respectively.
- Based on the relation between the spatial distribution of the pesticides and their soil sorption capacities, the highly dispersed distribution of dichlorvos compared to the other pesticides was associated with its remarkably low Koc value of 50, which implies a “very mobile” physicochemical characteristic. Furthermore, the relatively low spatial distribution of imidacloprid, diflubenzuron, 4,4'-DDD, permethrin, fenpropathrin, HCH, fenthion, prothiofos, chlorfenapyr, diflufenican, bifenox, aclonifen, ethalfluralin, fenpropimorph, and HCB pesticides was determined as strongly compatible with their considerably high soil sorption capacities, which correspond to immobile characteristics in the environment.
- Since imidacloprid, diflubenzuron, 4,4'-DDD, permethrin, fenpropathrin, HCH, fenthion, prothiofos, chlorfenapyr, diflufenican, bifenox, aclonifen, ethalfluralin, fenpropimorph and HCB have characteristics of low mobility or complete immobility in the environment, the occurrence of these 15 pesticides was attributed to the agricultural activities that are performed in

the vicinity environment of the polluted site rather than agricultural activities performed in remote areas.

- Based on the assessment of the relation between the detection frequencies of the pesticides and their water and soil half-lives, it was determined that the contribution of the recent pesticide spraying activities to the occurrence of the 16 pesticides in the river is predominant compared to the contribution of historical pesticide spraying activities performed in the river basin.
- The most frequent detections of insecticides, herbicides, and fungicides were observed in August, April, and October, respectively.
- The drastic upward trend in the precipitation amount from August to October in the river basin was positively correlated with the sharply increasing trend of the number of total pesticide detections from the August to October sampling period.
- The temporal precipitation trend of the river basin was determined as generally compatible with the monthly occurrence trend of the pesticides in the river basin. This compatibility shows the active role of the precipitation factor as an effective driving force in the occurrence of pesticides in the river basin.

As a suggestion for future research, the current status of the pesticide pollution at the target fields need to be validated by larger water quality data, which comprise the sampling studies of all months of the year. Since the localized climate is one of the most influential components of pesticide dissemination mechanism, the examination of climatic conditions can involve detailed localized climate components in future studies. In this regard, future research can further develop source identification by integrating the impact of localized severity and direction of the wind on the sprayed drift of pesticides from application lands to the river. Besides, the impact of localized temperature on the evaporation of pesticides and entrance into the river by atmospheric deposition can be investigated by advanced modeling and analysis techniques. Since the slope of the terrain is also one the driving force that has the potential to trigger the sweep of pesticides to the river, the assessment of the impact of land slope on pesticide occurrences in the river can also be taken into account as a part of the research. The texture and type of the soil can determine whether pesticides will infiltrate through the soil and reach the groundwater or will be washed through the surface runoff. Therefore, the relation between the soil type of the study area and the pesticide occurrences can be investigated within the context of the investigation of pesticide occurrence in the river. Another limitation of this study was the uncertainties regarding the exact locations of the water quality sampling stations. Even though the information of the districts where sampling stations are located is available, the exact location of the sampling stations in the boundaries of each district is questionable; therefore, it is recommended to resolve and clarify the uncertainties related to the distance between the individual agricultural fields and the observation site of the pesticide pollution.

CHAPTER 4

CONCLUDING REMARKS

In this thesis, metal pollution and pesticide pollution, as being two different environmental issues of the Yeşilırmak River Basin were addressed by focusing on target-specific assessment and analysis approaches. Within the context of the analysis and assessment of the metal pollution, basin-specific NBCs were derived, and basin-specific EQSs were established for 26 metals and metalloids observed in the Yeşilırmak River Basin by following conservative data analysis in order to attain reliable and realistic results. In this respect, pre-treatment and compilation of data, outlier test by Adjusted Tukey's Method, below-LOD treatment by introducing three different approaches, and low percentile analysis were implemented by using the concentration data of each metal and metalloid observed in the Yeşilırmak River Basin. Within the scope of the analysis and assessment of pesticide pollution, agricultural sources of pesticide pollution in the Yeşilırmak River Basin were identified for each district where sampling stations are located. For the fulfillment of the target-oriented source identification of the pesticide pollution observed in the river basin, the localized geographic and climatic conditions and agricultural profiles were taken into account individually for each district of the river basin. In order to achieve this goal, first of all, the information on the type, spraying frequency, and spraying timing of the agrochemicals against to the crop-specific pests were obtained by individually contacting the agricultural engineers of the District Directorates of Agriculture and Forestry of the 26 districts that locate water quality sampling stations in their boundaries. Within the light of the site-oriented expert knowledge on district-specific agricultural activities, detailed inventories were prepared by gathering and compiling information on district-specific agricultural characteristics and the localized insecticide, herbicide, and fungicide spraying schedules of each crop type raised in each district of the river basin. After the preparation of crop based district-specific inventories, the dominant crops raised in each district of the river basin were identified by calculating the areal shares of each crop type at district scale and basin scale. After the identification of the dominant crops for each district, the type and pollution degree of the pesticides that exceeded their EQS values at the sampling stations of each district were analyzed and determined by pursuing district-specific assessments. After these analysis and assessments, the temporal correlations between the agricultural activities and the pesticide occurrences observed at the sampling stations of each district were established and, crop based agricultural sources of the pesticide pollution were identified for each district of the river basin. In addition, spatial distribution pattern and temporal occurrence trend of the pesticides across the Yeşilırmak River Basin were analyzed and assesed by taking into account the impact of precipitation, district altitude, mobility of pesticides and water and soil half-lives of pesticides on their occurrence in the river. In this context, the relation between the precipitation trend and temporal occurrence trend of the pesticides in the river basin were analyzed and determined. Furthermore, the impact of the persistence and mobility of the pesticides on their spatial and temporal concentration trends were analyzed and examined by taking into account the assessment of the soil sorption capacity, water half-life and soil half-life of each pesticide. Besides, the relation between the altitudes of the districts and the diversity of the pesticide types that were observed at the sampling stations of the corresponding districts were analyzed and determined within the scope of this thesis.

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APPENDICES

A. AVERAGE, MAXIMUM AND EQS VALUES OF PESTICIDES AT EACH SAMPLING STATION

Table 4.1 Average and Maximum Concentrations of Pesticides at 42 Sampling Stations and Their EQS Values

Sampling Station	*Pesticides	AA-EQS, µg/L	Average Value, µg/L	MAC-EQS, µg/L	Maximum Value, µg/L
Y-1	Dichlorvos	0.0006	0.035	0.0007	0.150
	4,4'-DDD	0.025	0.005	0.025	0.040
	Endrin	0.010	0.007	-	0.040
	Permethrin	0.120	0.072	0.120	0.540
	Diflubenzuron	0.130	0.039	0.130	0.140
	Diflufenican	0.010	0.012	0.010	0.060
	Fenpropimorph	0.100	0.085	30	0.330
Y-2	Bifenox	0.012	0.045	0.040	0.186
	Dichlorvos	0.0006	0.033	0.0007	0.204
Y-3	Aclonifen	0.120	0.073	0.120	0.570
	Dichlorvos	0.0006	0.009	0.0007	0.068
	Atrazine-desethyl	0.300	0.227	3.000	0.613
	Cadusafos	0.010	0.006	0.020	0.015
	Fenpropathrin	0.010	0.012	0.010	0.061
Y-4	HCH	0.020	0.013	0.040	0.048
	Aclonifen	0.120	0.060	0.120	0.459
	Dichlorvos	0.0006	0.014	0.0007	0.113
	Atrazine-desethyl	0.300	0.190	3.000	0.319
	Diflubenzuron	0.130	0.045	0.13	0.182
	Prothiofos	0.100	0.067	16	0.359
Y-5	HCH	0.020	0.005	0.040	0.022
	Bifenox	0.012	0.011	0.040	0.068
	Dichlorvos	0.0006	0.027	0.0007	0.165

Table 4.1 (cont'd)

Sampling Station	*Pesticides	AA-EQS, µg/L	Average Value, µg/L	MAC-EQS, µg/L	Maximum Value, µg/L
	Ethalfluralin	0.300	0.171	0.500	1.350
Y-6	HCH	0.020	0.012	0.040	0.049
	Dichlorvos	0.0006	0.015	0.0007	0.072
	Fenthion	0.050	0.060	1.100	0.201
	Cyromazine	0.200	0.062	16	0.212
	Diflubenzuron	0.130	0.063	0.130	0.215
	Ethalfluralin	0.300	0.120	0.500	0.590
Y-7	HCH	0.020	0.006	0.040	0.020
	Dichlorvos	0.0006	0.028	0.0007	0.107
	Atrazine-desethyl	0.300	0.203	3	0.421
Y-8	Dichlorvos	0.0006	0.033	0.0007	0.143
	Fenthion	0.050	0.073	1.1	0.408
	Fenpropimorph	0.100	0.179	30	1.086
Y-9	Dichlorvos	0.0006	0.050	0.0007	0.295
	Chlorsulfuron	0.020	0.013	0.6	0.030
Y-10	HCH	0.020	0.005	0.04	0.026
	Aclonifen	0.120	0.041	0.12	0.312
	Dichlorvos	0.0006	0.030	0.0007	0.143
	Ethalfluralin	0.300	0.056	0.5	0.433
Y-11	Aclonifen	0.120	0.049	0.12	0.375
	Atrazine-desethyl	0.300	0.213	3	0.501
	Ethalfluralin	0.300	0.131	0.5	1.029
	Prothiofos	0.100	0.035	16	0.103
Y-12	HCB	-	0.013	0.05	0.098
	Dichlorvos	0.0006	0.025	0.0007	0.107
	Atrazine-desethyl	0.300	0.253	3	0.821
	Chlorsulfuron	0.02	0.012	0.6	0.027
	Diflubenzuron	0.13	0.054	0.13	0.255
Y-13	HCH	0.02	0.006	0.04	0.027
	Dichlorvos	0.0006	0.012	0.0007	0.098
	Atrazine-desethyl	0.3	0.240	3	0.721
	Chlorsulfuron	0.02	0.014	0.6	0.043
	Prothiofos	0.1	0.071	16	0.369
Y-14	Aclonifen	0.12	0.131	0.12	0.645

Table 4.1 (cont'd)

Sampling Station	***Pesticides**	**AA-EQS, µg/L**	**Average Value, µg/L**	**MAC-EQS, µg/L**	**Maximum Value, µg/L**
	Chlorsulfuron	0.02	0.015	0.6	0.037
	Diflubenzuron	0.13	0.085	0.13	0.323
	Ethalfluralin	0.3	0.196	0.5	0.968
	Prothiofos	0.1	0.066	16	0.231
Y-15	Bifenox	0.012	0.037	0.04	0.280
	Dichlorvos	0.0006	0.009	0.0007	0.067
	Diflubenzuron	0.13	0.046	0.13	0.195
	Ethalfluralin	0.3	0.135	0.5	1.066
	Fenpropimorph	0.1	0.102	30	0.464
	Prothiofos	0.1	0.071	16	0.353
Y-16	HCB	-	0.008	0.05	0.060
	HCH	0.02	0.005	0.04	0.022
	Aclonifen	0.12	0.052	0.12	0.395
	Dichlorvos	0.0006	0.010	0.0007	0.077
	Atrazine-desethyl	0.3	0.205	3	0.440
Y-17	Aclonifen	0.12	0.043	0.12	0.328
	Dichlorvos	0.0006	0.019	0.0007	0.153
	Diflubenzuron	0.13	0.061	0.13	0.311
	Prothiofos	0.1	0.067	16	0.315
Y-18	HCH	0.02	0.008	0.04	0.048
	Aclonifen	0.12	0.045	0.12	0.340
	Dichlorvos	0.0006	0.010	0.0007	0.080
	Diflubenzuron	0.13	0.093	0.13	0.567
	Fenpropimorph	0.1	0.083	30	0.317
	Prothiofos	0.1	0.101	16	0.631
Y-19	HCB	-	-	0.05	1.379
	Dichlorvos	0.0006	0.075	0.0007	0.343
	Diflubenzuron	0.13	0.041	0.13	0.154
	Prothiofos	0.1	0.149	16	1.013
Y-20	Bifenox	0.012	0.016	0.04	0.111
	Dichlorvos	0.0006	0.013	0.0007	0.075
	Chlorfenapyr	0.007	0.003	0.4	0.008
	Cyromazine	0.2	0.048	16	0.208
	Prothiofos	0.1	0.549	16	4.161
Y-21	HCH	0.02	0.017	0.04	0.120
	Dichlorvos	0.0006	0.017	0.0007	0.133
	DDT total	0.01	0.004	0.65	0.017

Table 4.1 (cont'd)

Sampling Station	*Pesticides	AA-EQS, µg/L	Average Value, µg/L	MAC-EQS, µg/L	Maximum Value, µg/L
	Atrazine-desethyl	0.3	0.224	3	0.592
	Diflubenzuron	0.13	0.044	0.13	0.181
	Fenpropimorph	0.1	0.090	30	0.372
Y-22	HCH	0.02	0.005	0.04	0.024
	Bifenox	0.012	0.020	0.04	0.145
	Dichlorvos	0.0006	0.031	0.0007	0.246
	Atrazine-desethyl	0.3	0.249	3	0.792
	Diflubenzuron	0.13	0.051	0.13	0.231
Y-23	Bifenox	0.012	0.027	0.04	0.197
	Dichlorvos	0.0006	0.017	0.0007	0.136
	Chlorsulfuron	0.02	0.015	0.6	0.052
	Ethalfluralin	0.3	0.079	0.5	0.615
Y-24	HCH	0.02	0.012	0.04	0.067
	Dichlorvos	0.0006	0.012	0.0007	0.081
	Chlorsulfuron	0.02	0.014	0.6	0.036
	Diflubenzuron	0.13	0.281	0.13	1.815
	Imidacloprid	0.14	0.074	1.4	0.314
Y-25	Aclonifen	0.12	0.054	0.12	0.415
	Dichlorvos	0.0006	0.046	0.0007	0.256
	Chlorsulfuron	0.02	0.015	0.6	0.049
	Diflubenzuron	0.13	0.065	0.13	0.346
	Fenpropimorph	0.1	0.271	30	1.819
	Imidacloprid	0.14	0.152	1.4	0.671
Y-26	HCH	0.02	0.011	0.04	0.072
	Aclonifen	0.12	0.076	0.12	0.594
	Dichlorvos	0.0006	0.011	0.0007	0.086
	Chlorfenapyr	0.007	0.008	0.4	0.044
	Chlorsulfuron	0.02	0.015	0.6	0.048
	Diflubenzuron	0.13	0.054	0.13	0.254
	Diflufenican	0.01	0.006	0.01	0.015
	Ethalfluralin	0.3	0.042	0.5	0.316
Y-27	HCH	0.02	0.025	0.04	0.180
	Aclonifen	0.12	0.047	0.12	0.357
	Bifenox	0.012	0.016	0.04	0.108
	Dichlorvos	0.0006	0.013	0.0007	0.105
	Chlorsulfuron	0.02	0.015	0.6	0.046

Table 4.1 (cont'd)

Sampling Station	*Pesticides	AA-EQS, µg/L	Average Value, µg/L	MAC-EQS, µg/L	Maximum Value, µg/L
	Ethalfluralin	0.3	0.049	0.5	0.377
Y-28	Dichlorvos	0.0006	0.093	0.0007	0.462
Y-29	HCH	0.02	0.013	0.04	0.083
	Dichlorvos	0.0006	0.011	0.0007	0.084
	Chlorsulfuron	0.02	0.012	0.6	0.028
	Diflubenzuron	0.13	0.075	0.13	0.427
Y-30	Dichlorvos	0.0006	0.374	0.0007	0.374
Y-31	Chlorpyrifos	0.03	0.009	0.1	0.033
	Hekzakloro-siklohekzan	0.02	0.005	0.04	0.024
	Dichlorvos	0.0006	0.032	0.0007	0.252
	Chlorsulfuron	0.02	0.013	0.6	0.034
Y-32	Bifenox	0.012	0.034	0.04	0.225
	Dichlorvos	0.0006	0.083	0.0007	0.427
	Fenthion	0.05	0.051	1.1	0.208
	Chlorfenapyr	0.007	0.004	0.4	0.011
	Chlorsulfuron	0.02	0.012	0.6	0.027
	Diflubenzuron	0.13	0.369	0.13	2.432
	Ethalfluralin	0.3	0.062	0.5	0.421
	Fenpropimorph	0.1	0.147	30	0.731
	Nicosulfuron	0.05	0.020	0.2	0.081
Y-33	HCB	-		0.05	0.079
	HCH	0.02	0.018	0.04	0.107
	Bifenox	0.012	0.031	0.04	0.228
	Dichlorvos	0.0006	0.021	0.0007	0.163
	Fenthion	0.05	0.053	1.1	0.252
	Atrazine-desethyl	0.3	0.268	3	0.940
	Diflubenzuron	0.13	0.043	0.13	0.172
	Ethalfluralin	0.3	0.083	0.5	0.649
Y-34	HCH	0.02	0.006	0.04	0.030
	Dichlorvos	0.0006	0.024	0.0007	0.169
	Chlorothalonil	0.3	0.051	4.2	0.326
	Chlorsulfuron	0.02	0.013	0.6	0.034
	Diflubenzuron	0.13	0.078	0.13	0.396
	Diflufenican	0.01	0.007	0.01	0.018
	Ethalfluralin	0.3	0.088	0.5	0.600
Y-35	Dichlorvos	0.0006	0.016	0.0007	0.126

Table 4.1 (cont'd)

Sampling Station	*Pesticides	AA-EQS, µg/L	Average Value, µg/L	MAC-EQS, µg/L	Maximum Value, µg/L
	Chlorothalonil	0.3	0.065	4.2	0.481
	Cyromazine	0.2	0.048	16	0.206
	Diflufenican	0.01	0.008	0.01	0.025
	Ethalfluralin	0.3	0.087	0.5	0.681
Y-36	HCB	-		0.05	0.323
	Dichlorvos	0.0006	0.009	0.0007	0.068
	Chlorothalonil	0.3	0.082	4.2	0.619
	Atrazine-desethyl	0.3	0.202	3	0.417
	Chlorsulfuron	0.02	0.016	0.6	0.056
	Ethalfluralin	0.3	0.201	0.5	1.591
Y-37	Bifenox	0.012	0.046	0.04	0.349
	Dichlorvos	0.0006	0.039	0.0007	0.218
	Azinphos-methyl	0.05	0.030	0.4	0.064
	Chlorothalonil	0.3	0.065	4.2	0.486
	Ethalfluralin	0.3	0.268	0.5	2.128
Y-39	HCH	0.02	0.007	0.04	0.035
	Aclonifen	0.12	0.073	0.12	0.565
	Dichlorvos	0.0006	0.012	0.0007	0.091
	Chlorothalonil	0.3	0.060	4.2	0.446
	Atrazine-desethyl	0.3	0.199	3	0.393
	Chlorsulfuron	0.02	0.013	0.6	0.033
	Ethalfluralin	0.3	0.176	0.5	1.392
Y-40	HCH	0.02	0.014	0.04	0.091
	Aclonifen	0.12	0.108	0.12	0.844
	Bifenox	0.012	0.032	0.04	0.236
	Dichlorvos	0.0006	0.017	0.0007	0.131
	Chlorothalonil	0.3	0.082	4.2	0.621
	Chlorsulfuron	0.02	0.018	0.6	0.073
	Ethalfluralin	0.3	0.412	0.5	3.279
Y-41	HCB		0.031	0.05	0.238
	Aclonifen	0.12	0.124	0.12	0.972
	Dichlorvos	0.0006	0.023	0.0007	0.179
	Diflubenzuron	0.13	0.041	0.13	0.157
	Ethalfluralin	0.3	0.184	0.5	1.453
Y-42	HCB			0.05	0.118

Table 4.1 (cont'd)

Sampling Station	*Pesticides	AA-EQS, µg/L	Average Value, µg/L	MAC-EQS, µg/L	Maximum Value, µg/L
	HCH	0.02	0.039	0.04	0.298
	Bifenox	0.012	0.020	0.04	0.146
	DDT total	0.01	0.004	0.65	0.017
	Chlorothalonil	0.3	0.061	4.2	0.453
	Atrazine-desethyl	0.3	0.191	3	0.331
	Chlorsulfuron	0.02	0.014	0.6	0.043
	Diflubenzuron	0.13	0.058	0.13	0.292
	Ethalfluralin	0.3	0.184	0.5	1.451
Y-43	Dichlorvos	0.0006	0.044	0.0007	0.308
	Chlorothalonil	0.3	0.059	4.2	0.382
	Ethalfluralin	0.3	0.488	0.5	3.404
	Thiacloprid	0.13	0.054	2	0.228

* The pesticides written in red letters have the concentration data that exceeded at least one of the AA-EQS and MAC-EQS values.

B. AGRICULTURAL SOURCE IDENTIFICATION OF PESTICIDE POLLUTION FOR SAMSUN PROVINCE

Ladik District of Samsun Province (Y-40 Sampling Station)

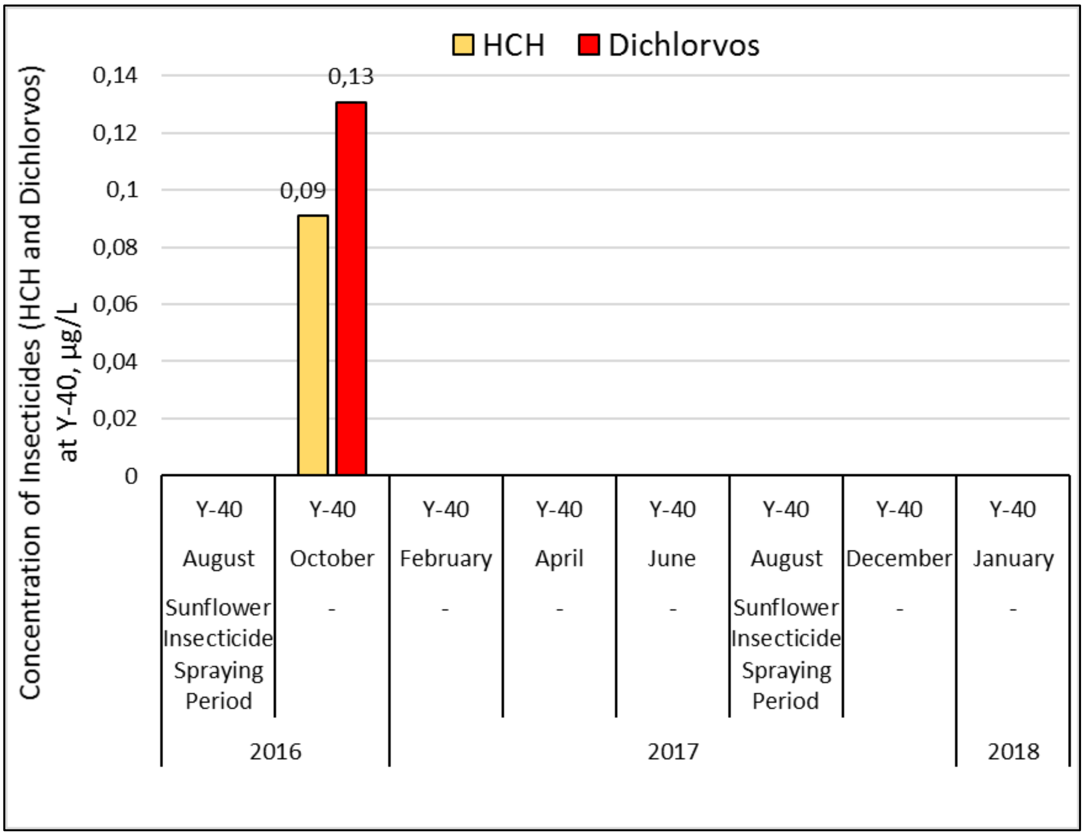

Figure 4.1 Correlation Between EQS Exceedance Months of Insecticides (at Y-40) and Insecticide Spraying Periods for the Dominant Crops of Ladik

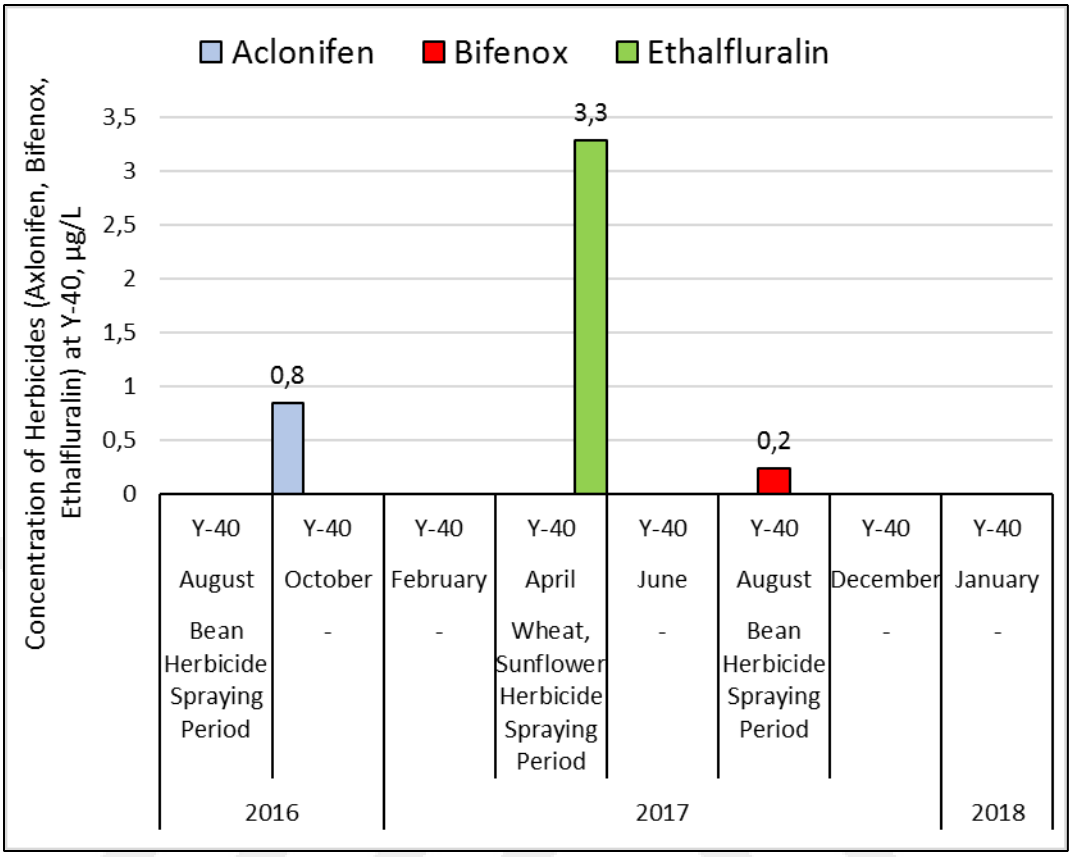

Figure 4.2 Correlation Between EQS Exceedance Months of Herbicides (at Y-40) and Herbicide Spraying Periods for the Dominant Crops of Ladik

Table 4.2 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-40 Sampling Station of Ladik

<table>
<tr><th rowspan="2">Stations</th><th rowspan="2">Pesticides</th><th colspan="2">EQS Exceedance %</th><th rowspan="2">Detection Frequency %</th><th rowspan="2">Potential Sources of the Observed Pesticides</th></tr>
<tr><th>AA-EQS</th><th>MAC-EQS</th></tr>
<tr><td rowspan="4">Y-40</td><td>Dichlorvos</td><td>2656</td><td>18549</td><td>12.5</td><td>Agricultural Source:
- Sunflower Farmland: 12940 da</td></tr>
<tr><td>Aclonifen</td><td>-</td><td>603</td><td>12.5</td><td rowspan="2">Agricultural Source:
- Bean Farmland:
6750 da</td></tr>
<tr><td>Bifenox</td><td>164</td><td>490</td><td>12.5</td></tr>
<tr><td>Ethalfluralin</td><td>37</td><td>555</td><td>12.5</td><td>Agricultural Source:
-Wheat Farmland:
80188 da
- Sunflower Farmland: 12940 da</td></tr>
</table>

İlkadım District of Samsun Province (Y-41 Sampling Station)

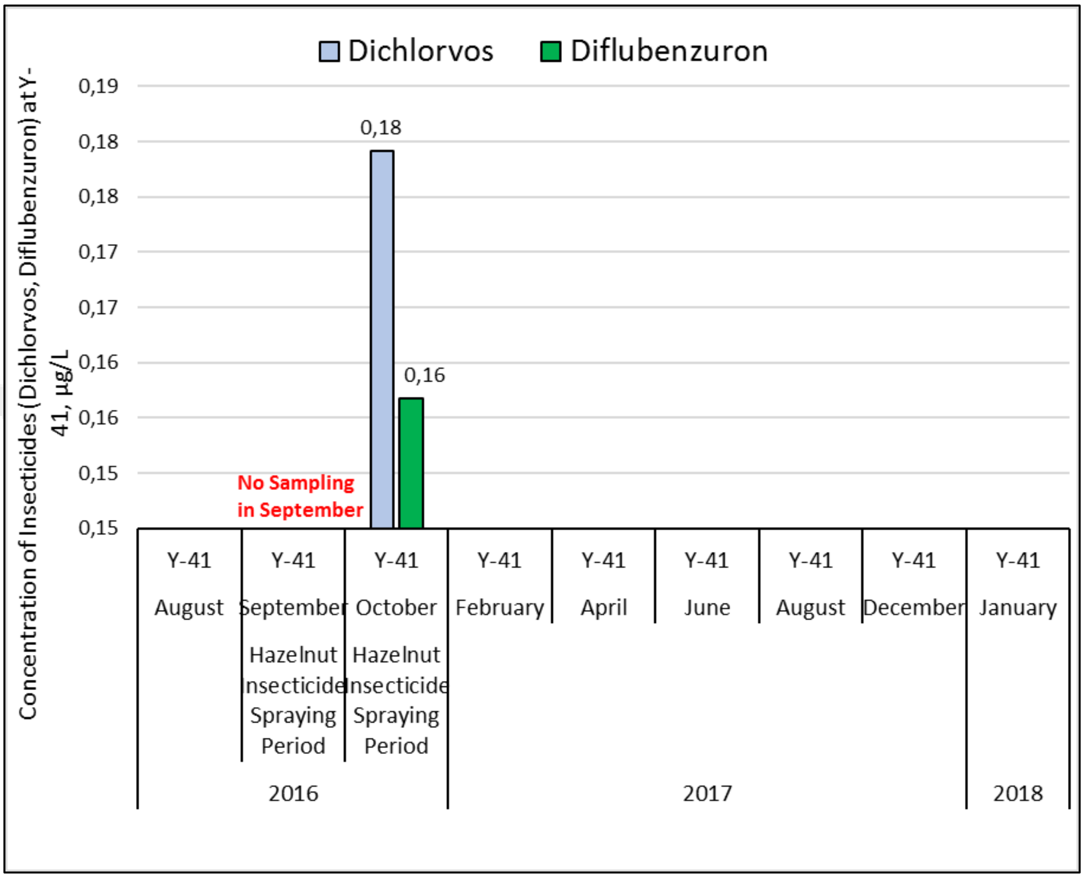

Figure 4.3 Correlation Between EQS Exceedance Months of Insecticides (at Y-41) and Insecticide Spraying Periods for the Dominant Crops of İlkadım

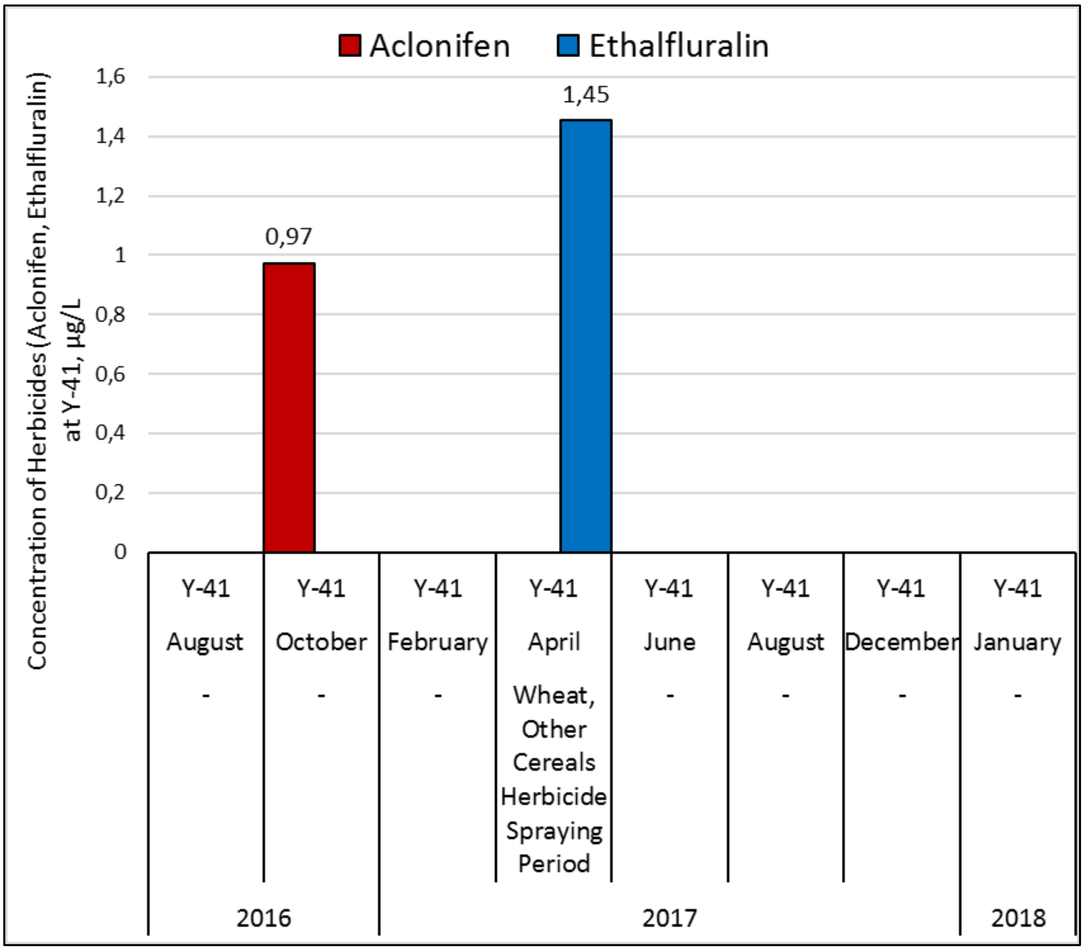

Figure 4.4 Correlation Between EQS Exceedance Months of Herbicides (at Y-41) and Herbicide Spraying Periods for the Dominant Crops of İlkadım

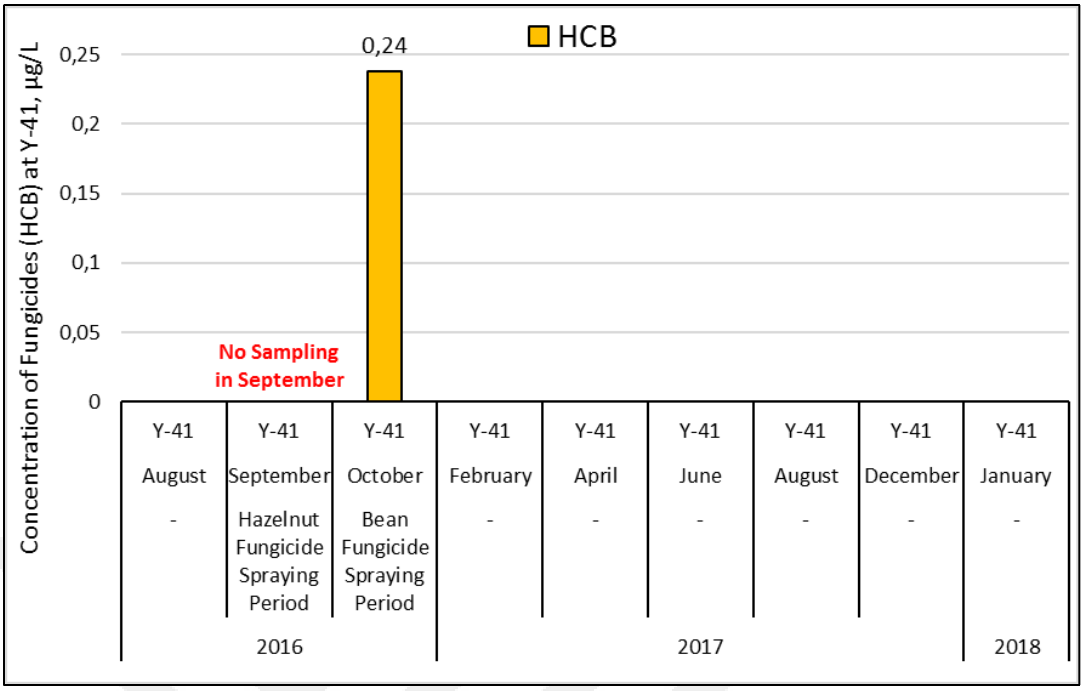

Figure 4.5 Correlation Between EQS Exceedance Months of Fungicides (at Y-41) and Fungicide Spraying Periods for the Dominant Crops of İlkadım

Table 4.3 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-41 Sampling Station of İlkadım

Stations	Pesticides	EQS Exceedance %		Detection Frequency %	Potential Sources of the Observed Pesticides
		AA-EQS	MAC-EQS		
Y-41	Dichlorvos	3669	25495	12.5	**Agricultural Source:** - Hazelnut Farmland: 5300 da
	Diflubenzuron	-	21	12.5	
	Aclonifen	3	710	12.5	**Agricultural Source:** - Not Exist
	Ethalfluralin	-	191	12.5	**Agricultural Source:** - Wheat Farmland: 22379 da
	HCB	-	376	25	**Agricultural Source:** - Bean Farmland: 1400 da - Hazelnut Farmland: 5300 da

Çarşamba District of Samsun Province (Y-42 and Y-43 Sampling Stations)

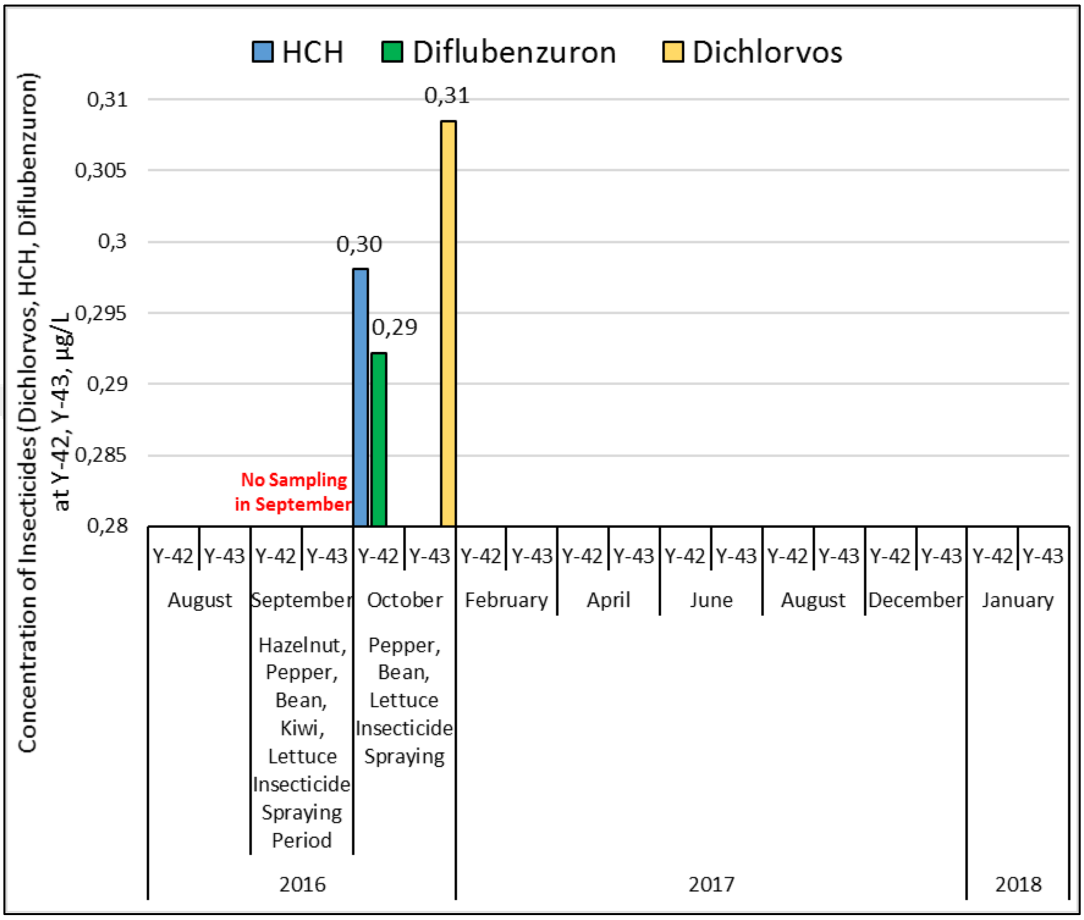

Figure 4.6 Correlation Between EQS Exceedance Months of Insecticides (at Y-42 and Y-43) and Insecticide Spraying Periods for the Dominant Crops of Çarşamba

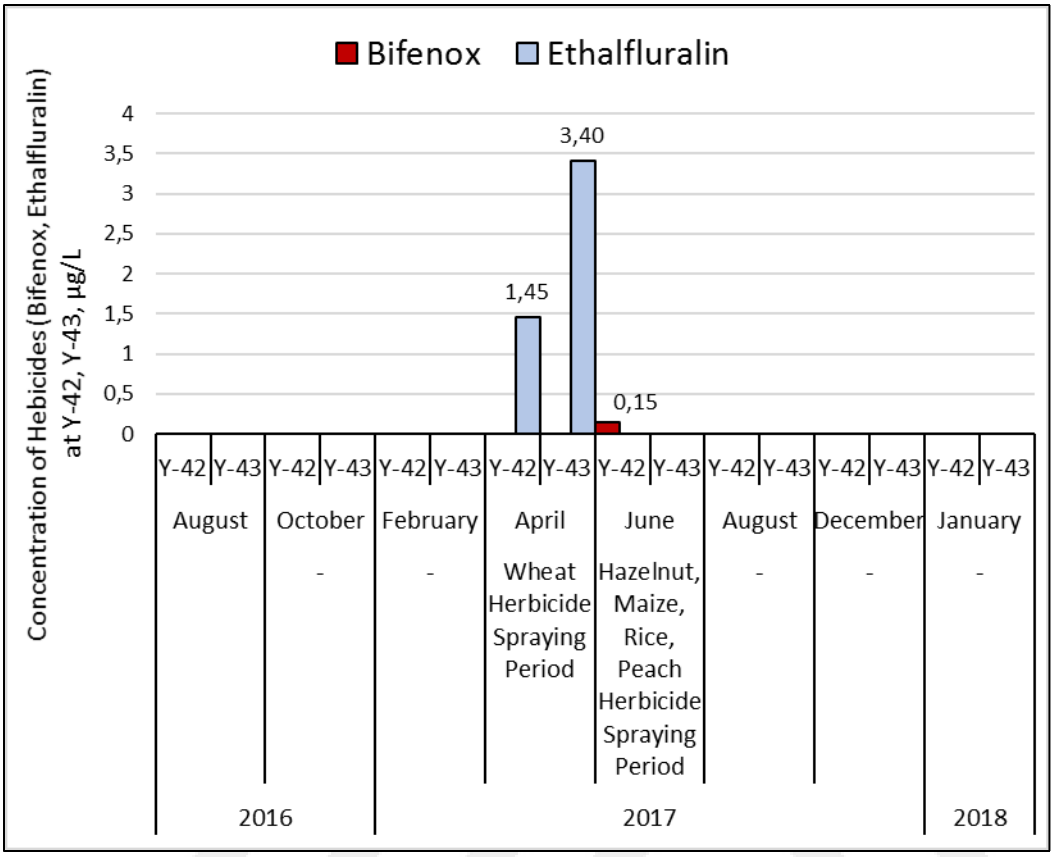

Figure 4.7 Correlation Between EQS Exceedance Months of Herbicides (at Y-42 and Y-43) and Herbicide Spraying Periods for the Dominant Crops of Çarşamba

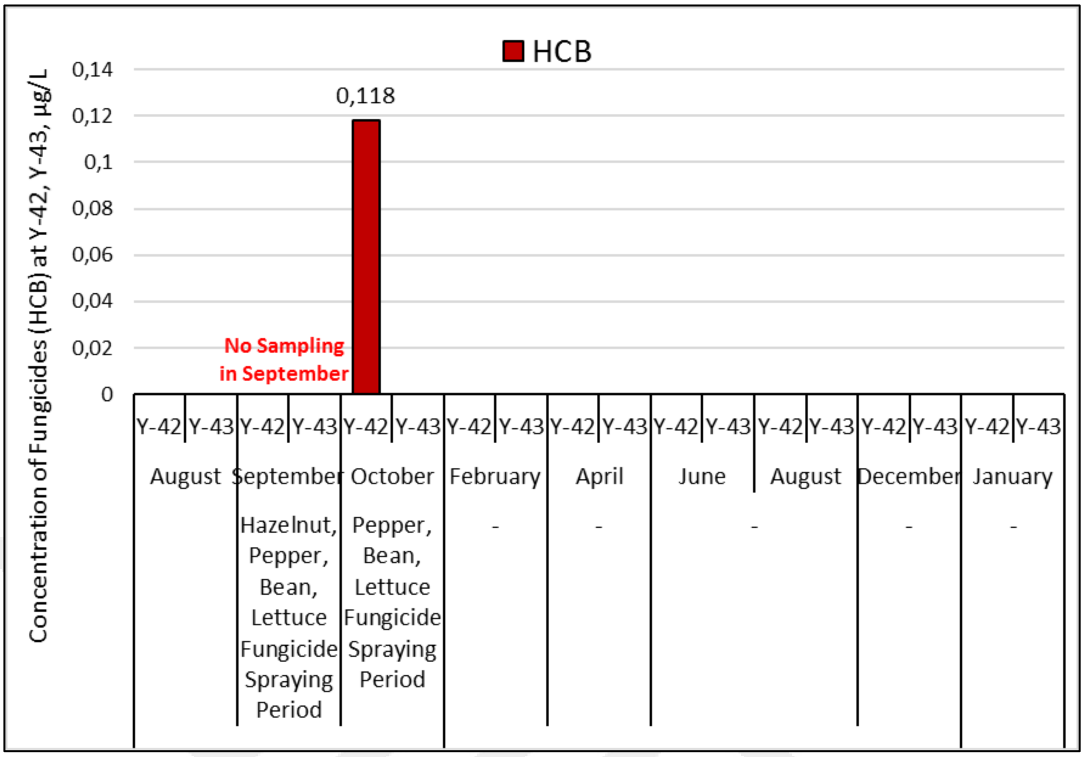

Figure 4.8 Correlation Between EQS Exceedance Months of Fungicides (at Y-42 and Y-43) and Fungicide Spraying Periods for the Dominant Crops of Çarşamba

Table 4.4 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-42 and Y-43 Sampling Station of Çarşamba

Stations	**Pesticides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Pesticides**
		AA-EQS	**MAC-EQS**		
Y-42	HCH	97	645	12.5	**Agricultural Sources:** -Hazelnut: 455500 da -Pepper: 8676 da -Bean: 4080 da -Lettuce: 1970 da -Kiwi: 2500 da
	Diflubenzuron	-	125	12.5	
Y-43	Dichlorvos	7280	43967	14.3	
Y-42	Bifenox	70	265	12.5	**Agricultural Sources:** -Hazelnut: 455500 da -Maize: 47952 da -Rice: 7849 da -Peach: 6000 da
	Ethalfluralin	-	190	12.5	**Agricultural Sources:** -Wheat: 6394 da
Y-43	Ethalfluralin	63	581	14.3	
Y-42	HCB	-	136	25	**Agricultural Sources:** -Hazelnut: 455500 da -Pepper: 8676 da -Bean: 4080 -Lettuce: 1970 da

C. AGRICULTURAL SOURCE IDENTIFICATION OF PESTICIDE POLLUTION FOR CORUM PROVINCE (MERKEZ AND ALACA DISTRICTS)

Merkez District of Çorum Province (Y-25, Y-26, Y-29 and Y-30 Sampling Stations)

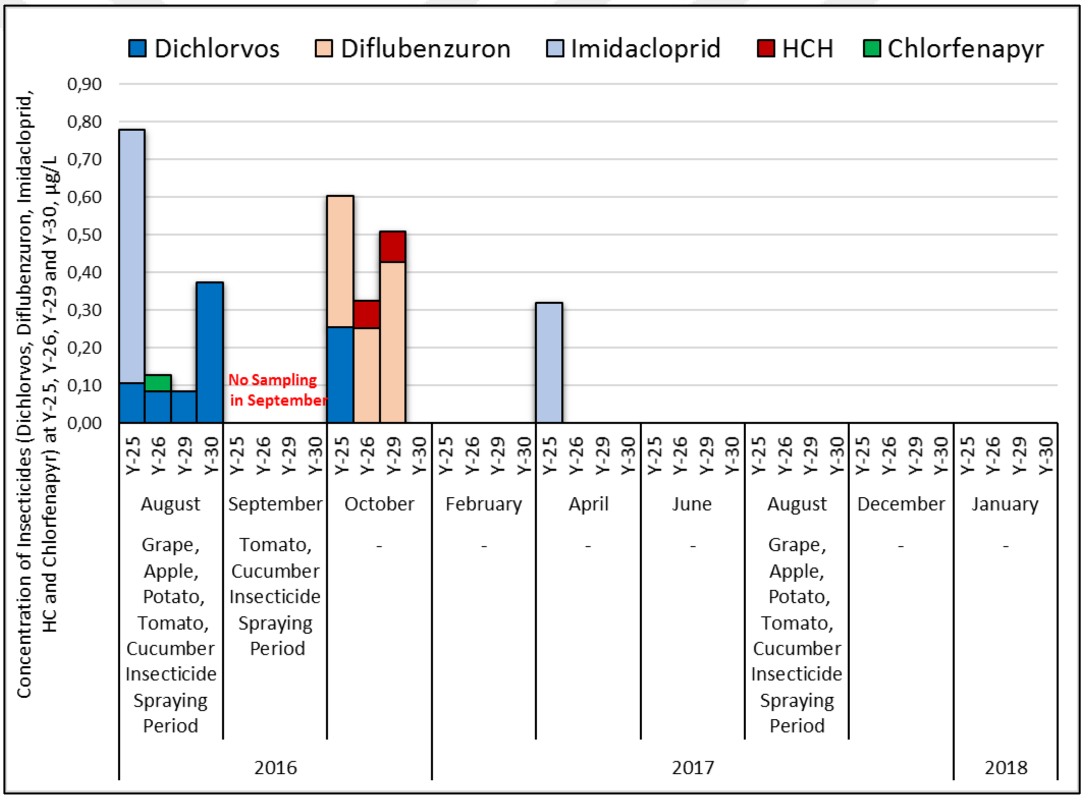

Figure 4.9 Correlation Between EQS Exceedance Months of Insecticides (at Y25, Y-26, Y-29 and Y-30) and Insecticide Spraying Periods for the Dominant Crops of Merkez-Çorum

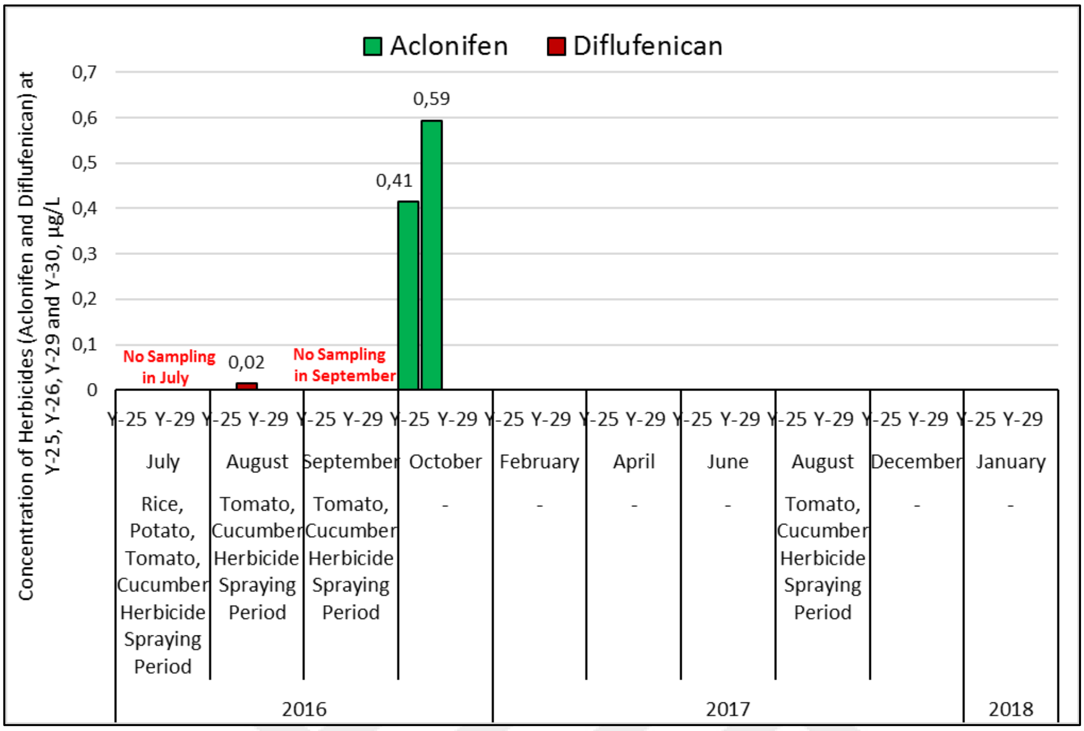

Figure 4.10 Correlation Between EQS Exceedance Months of Herbicides (at Y25, Y-26, Y-29 and Y-30) and Herbicide Spraying Periods for the Dominant Crops of Merkez-Çorum

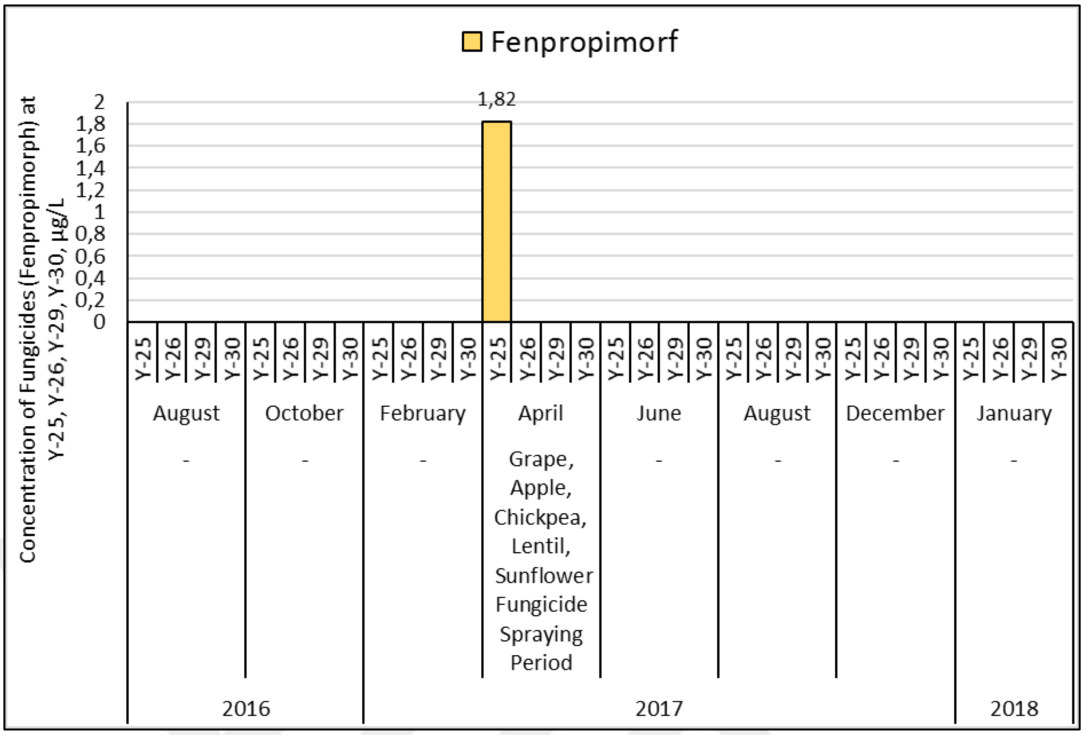

Figure 4.11 Correlation Between EQS Exceedance Months of Fungicides (at Y25, Y-26, Y-29 and Y-30) and Fungicide Spraying Periods for the Dominant Crops of Merkez-Çorum

Table 4.5 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-25 and Y-26, Y-29 and Y-30 Sampling Stations of Merkez-Çorum

<table>
<tr><th rowspan="2">Station</th><th rowspan="2">Pesticides</th><th colspan="2">EQS Exceedance %</th><th rowspan="2">Detection Frequency %</th><th rowspan="2">Potential Sources of the Observed Pesticides</th></tr>
<tr><th>AA-EQS</th><th>MAC-EQS</th></tr>
<tr><td rowspan="3">Y-25</td><td>Dichlorvos</td><td>7514</td><td>36524</td><td>25.0</td><td rowspan="11">- Grape: 7558 da
- Apple: 1745 da
- Tomato: 3821 da
- Potato: 8000 da
- Cucumber: 1236 da</td></tr>
<tr><td>Diflubenzuron</td><td>-</td><td>166</td><td>12.5</td></tr>
<tr><td>Imidacloprid</td><td>8</td><td>-</td><td>62.5</td></tr>
<tr><td rowspan="4">Y-26</td><td>Dichlorvos</td><td>1719</td><td>12123</td><td>12.5</td></tr>
<tr><td>HCH</td><td>-</td><td>81</td><td>12.5</td></tr>
<tr><td>Chlorfenapyr</td><td>10</td><td>-</td><td>12.5</td></tr>
<tr><td>Diflubenzuron</td><td>-</td><td>95</td><td>12.5</td></tr>
<tr><td rowspan="3">Y-29</td><td>HCH</td><td>-</td><td>108</td><td>12.5</td></tr>
<tr><td>Dichlorvos</td><td>1693</td><td>11942</td><td>12.5</td></tr>
<tr><td>Diflubenzuron</td><td>-</td><td>228</td><td>12.5</td></tr>
<tr><td>Y-30</td><td>Dichlorvos</td><td>62205</td><td>53304</td><td>100</td></tr>
<tr><td>Y-25</td><td>Aclonifen</td><td>-</td><td>246</td><td>12.5</td><td rowspan="2">Tomato: 3821 da
Cucumber: 1236 da</td></tr>
<tr><td rowspan="2">Y-26</td><td>Aclonifen</td><td>-</td><td>395</td><td>12.5</td></tr>
<tr><td>Diflufenican</td><td>-</td><td>50</td><td>12.5</td><td>Rice: 930 da
Tomato: 3821 da
Potato: 8000 da
Cucumber: 1236 da</td></tr>
<tr><td>Y-25</td><td>Fenpropimorph</td><td>171</td><td>-</td><td>12.5</td><td>Sunflower: 104994
Chickpea: 20000
Grape: 7558
Apple: 1745
Lentil: 3105</td></tr>
</table>

Alaca District of Çorum Province (Y-28 Sampling Station)

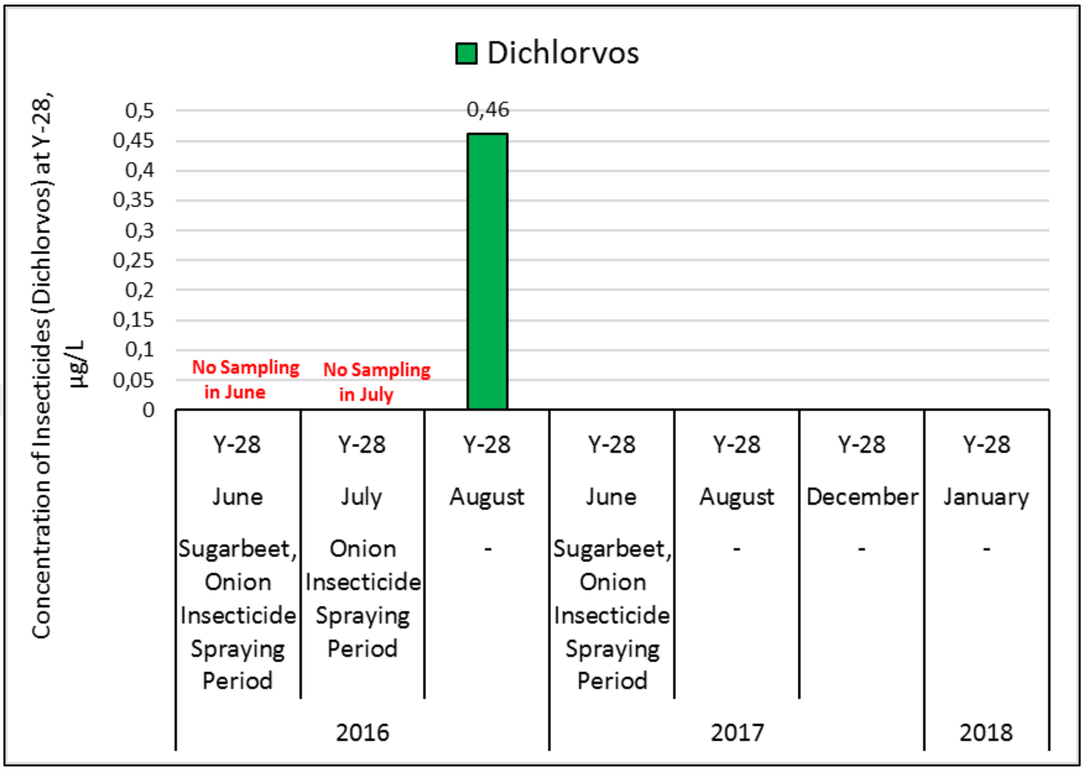

Figure 4.12 Correlation Between EQS Exceedance Months of Insecticides (at Y-28) and Insecticide Spraying Periods for the Dominant Crops of Alaca

Table 4.6 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-28 Sampling Station of Alaca

Station	**Pesticides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Pesticides**
		AA-EQS	**MAC -EQS**		
Y-28	Dichlorvos	2656	18549	12.5	**Agricultural Source:** - Sugarbeet: 15299 da -Onion: 12813 da

D. AGRICULTURAL SOURCE IDENTIFICATION OF PESTICIDE POLLUTION FOR YOZGAT PROVINCE (SARAYKENT AND AYDINCIK DISTRICTS)

Saraykent District of Yozgat Province (Y-15 Sampling Station)

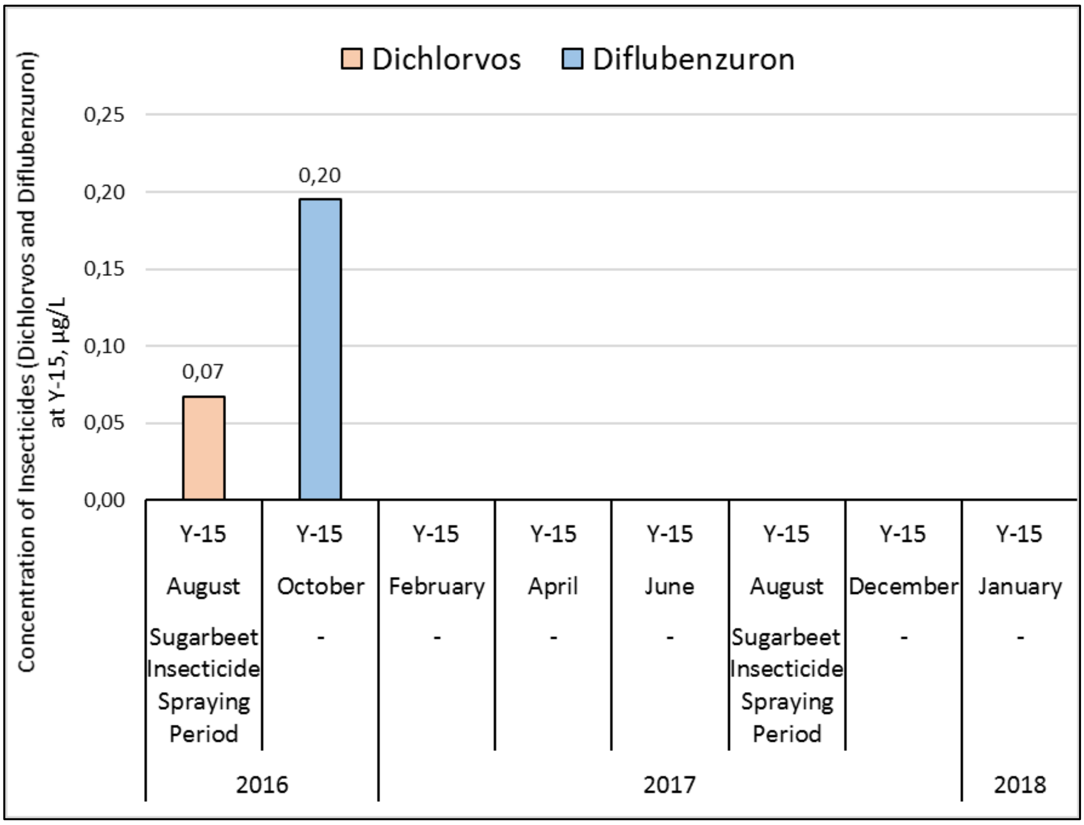

Figure 4.13 Correlation Between EQS Exceedance Months of Insecticides (at Y-15) and Insecticide Spraying Periods for the Dominant Crops of Saraykent

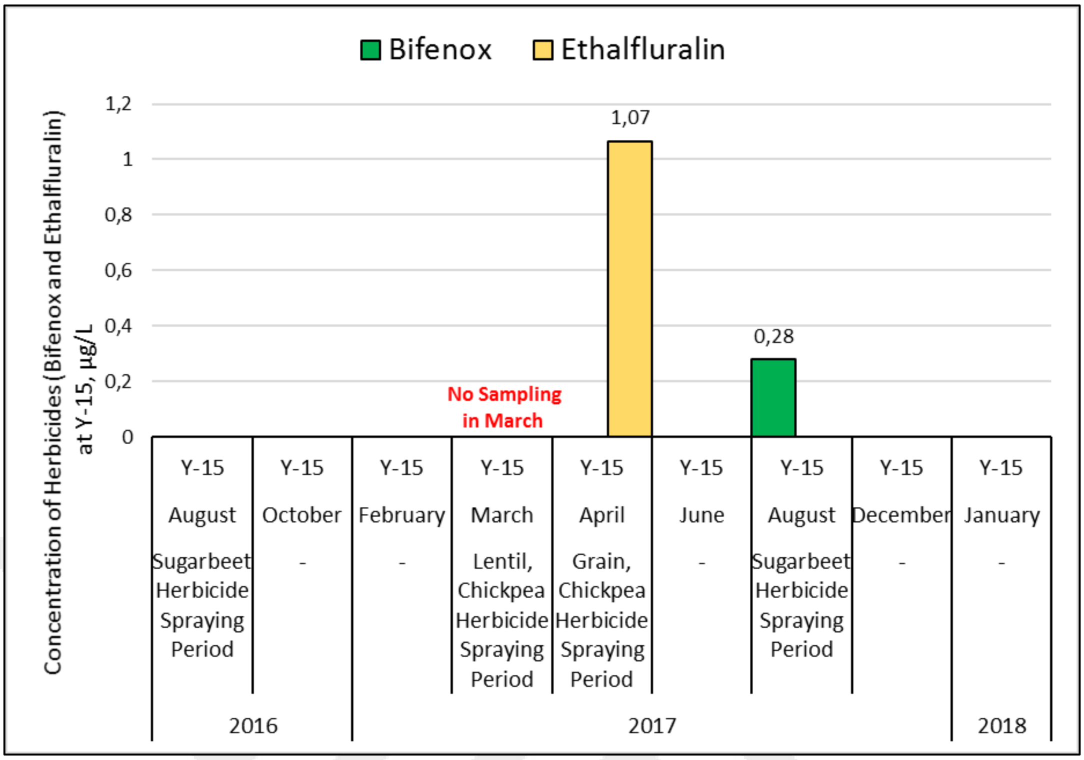

Figure 4.14 Correlation Between EQS Exceedance Months of Herbicides (at Y-15) and Herbicide Spraying Periods for the Dominant Crops of Saraykent

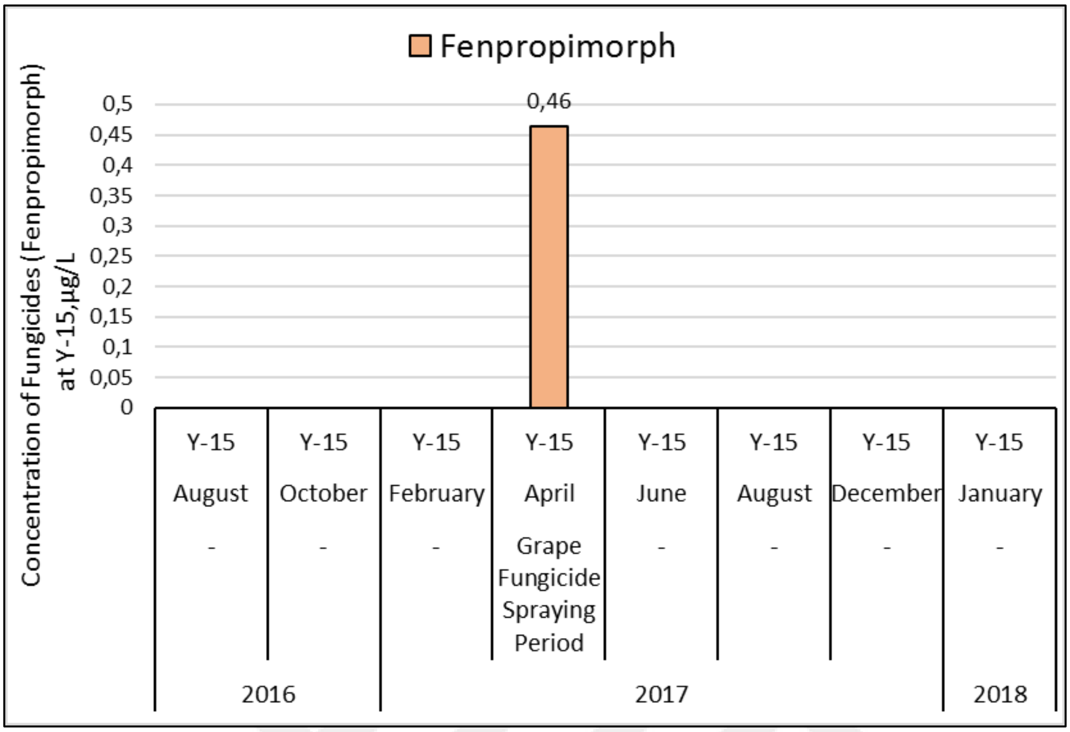

Figure 4.15 Correlation Between EQS Exceedance Months of Fungicides (at Y-15) and Fungicide Spraying Periods for the Dominant Crops of Saraykent

Table 4.7 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-15 Sampling Station of Saraykent

Station	**Pesticides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Pesticides**
		AA-EQS	**MAC-EQS**		
Y-15	Dichlorvos	1343	9542	12.5	**Agricultural Source:** -Sugarbeet: 512 da
	Diflubenzuron	-	50	12.5	
	Ethalfluralin	-	113	12.5	**Agricultural Source:** -Chickpea : 3000 da -Lentil: 1703 da -Wheat: 57956 da
	Bifenox	210	599	12.5	**Agricultural Source:** -Sugarbeet: 512 da
	Fenpropimorph	2	-	12.5	**Agricultural Source:** -Grape: 867 da

Aydıncık District of Yozgat Province (Y-27 Sampling Station)

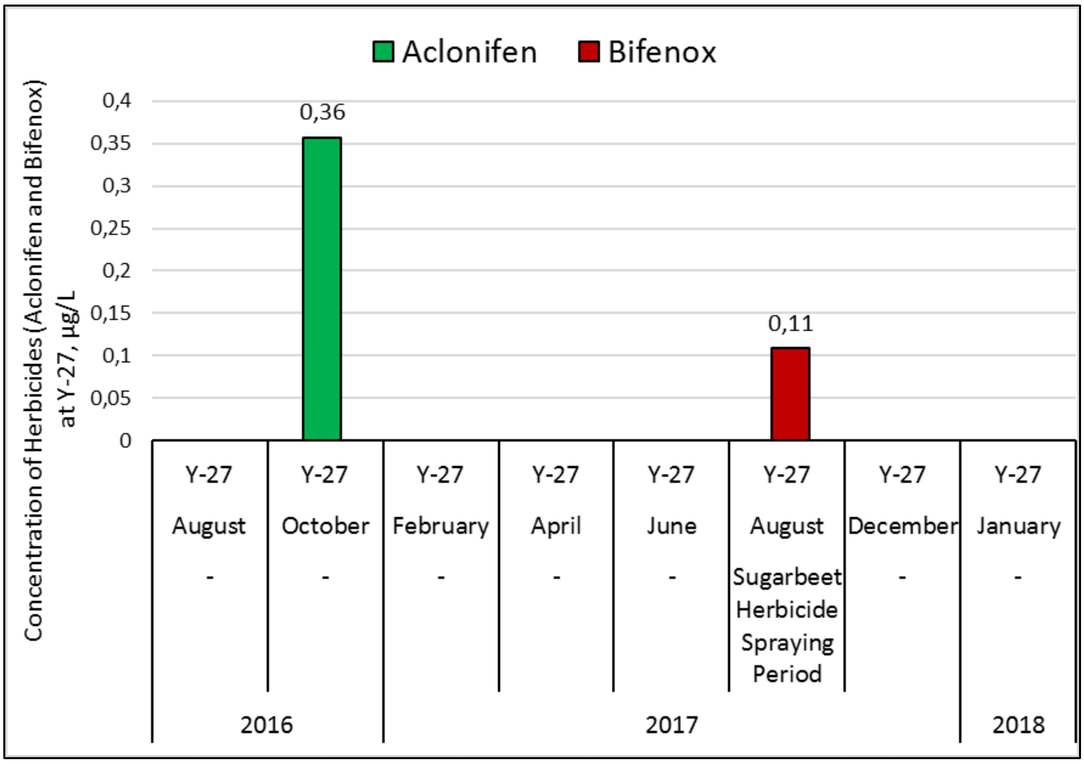

Figure 4.16 Correlation Between EQS Exceedance Months of Herbicides (at Y-27) and Herbicide Spraying Periods for the Dominant Crops of Aydıncık

Table 4.8 Potential Sources and Detection Percentages of the Pesticides Observed at the Y-27 Sampling Station of Aydıncık

Stations	**Pesticides**	**EQS Exceedance %**		**Detection Frequency %**	**Potential Sources of the Observed Pesticides**
		AA-EQS	**MAC-EQS**		
Y-27	HCH	24	351	12.5	**Agricultural Source:** - Not Exist
	Dichlorvos	2127	14918	12.5	
	Aclonifen	-	197	12.5	**Agricultural Source:** - Not Exist
	Bifenox	31	171	12.5	**Agricultural Source:** - Sugarbeet: 2661 da