THE FATE AND TRANSPORT OF SOME COMMONLY USED PESTICIDES IN THE KONYA PLAIN

by

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“The basis of the national economy is agriculture.”

Mustafa Kemal Atatürk

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ABSTRACT

THE FATE AND TRANSPORT OF COMMONLY USED PESTICIDES IN THE KONYA PLAIN

By protecting the agricultural products, pesticides are substances that are widely used worldwide to increase crop yields. Although pesticides can have beneficial effects on crop production, these chemicals have various adverse effects on human health, other living and environmental systems. By virtue of the aforementioned reasons, it is a necessity to understand the fate, transport and interactions of the pesticides in the natural systems. In this study, in order to investigate the fate and transport of two pesticides widely used in the Konya Plain (2,4-dichlorophenoxyacetic acid and fenoxaprop-p-ethyl), a series of batch sorption and column transport experiments were conducted. Soil samples collected from the Konya Plain were screened for a wide range of pesticides using liquid chromatography coupled with tandem mass spectroscopy (LC-MS/MS). Extraction of the pesticides from the soil samples was performed using "quick, easy, cheap, effective, rugged, and safe" QuEChERS method. Batch tests were conducted using selected soil samples to investigate the sorption potential of the target pesticides. Sorption kinetics as well as sorption isotherms were developed for the two pesticides. Column tests were conducted to evaluate the mobility potential of the target pesticides. Calibration curves with linear regression coefficients (R^2) greater than 0.990, were used for the estimation of distribution coefficients (K_d). The 24h K_d value of the Fenox was calculated as 297.4 mL g^{-1}. There was no significant K_d value calculated for 2,4-D. Overall, the experiments demonstrated that the transport potential of 2,4-D is high while Fenox mobility is limited due to its high sorption.

ÖZET

KONYA OVASI'NDAKİ BAZI BELLİ BAŞLI PESTİSİTLERİN AKIBETİ VE TAŞINMASI

Pestisitler, tarım ürünlerini koruyarak, mahsul verimini artırmak için dünya çapında yaygın olarak kullanılan maddelerdir. Pestisitlerin mahsul üretimi üzerinde faydalı etkileri olmasına rağmen, bu kimyasalların insan sağlığı, diğer canlılar ve çevre sistemleri üzerinde çeşitli olumsuz etkileri vardır. Yukarıda belirtilen nedenlerden dolayı pestisitlerin doğal sistemlerdeki akıbeti, taşınımı ve etkileşimlerinin anlaşılması bir zorunluluktur. Bu çalışmada, Konya Ovası'nda yaygın olarak kullanılan iki pestisitin (2,4-diklorofenoksiasetik asit ve fenoksaprop-p-etil) akıbetini ve taşınımını araştırmak amacıyla bir dizi sorpsiyon ve kolon taşıma deneyi yapılmıştır. Konya Ovası'ndan toplanan toprak numuneleri, tandem kütle spektroskopisi (LC-MS/MS) ile birleştirilmiş sıvı kromatografi kullanılarak çok çeşitli pestisitlerin varlığı taranmıştır. Pestisitlerin toprak örneklerinden ekstraksiyonu "hızlı, kolay, ucuz, etkili, sağlam ve güvenli" QuEChERS yöntemi kullanılarak gerçekleştirilmiştir. Hedef pestisitlerin sorpsiyon potansiyelini araştırmak için seçilen toprak örnekleri kullanılarak testler yapılmıştır. İki pestisit için sorpsiyon kinetiği ve sorpsiyon izotermleri geliştirilmiştir. Hedef pestisitlerin hareketlilik potansiyelini değerlendirmek için kolon testleri yapılmıştır. Dağılım katsayılarının (K_d) tahmininde doğrusal regresyon katsayıları (R^2) 0.990'dan büyük olan kalibrasyon eğrileri kullanılmıştır. Fenox'un 24h K_d değeri 297,4 mL g^{-1} olarak hesaplanmıştır. 2,4-D için hesaplanan anlamlı bir K_d değeri bulunamamıştır. Genel olarak deneyler, 2,4-D' nin taşınma potansiyelinin yüksek olduğunu gösterirken, yüksek sorpsiyona bağlı olarak Fenox mobilitesinin sınırlı olduğunu göstermiştir.

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LIST OF SYMBOLS/ABBREVIATIONS

Symbol	Explanation
%	Percent
µ	Micro
µL	Microliter
µg	Microgram
ng	Nanogram
g	Gram
°C	Degree Celsius

Abbreviation	Explanation
2,4-D	2,4-dichlorophenoxyacetic acid
ACN	Acetonitrile
AOAC	Association of Official Agricultural Chemists
APCI	Atmospheric pressure chemical-ionization
API	Atmospheric pressure-ionization
APPI	Atmospheric pressure photo-ionization
CEC	Cation Exchange Capacity
DDT	Dichlorodiphenyltrichloroethane
DNAPL	Dense Non-Aqueous Phase Liquid
dSPE	Dispersive Solid Phase Extraction
EA	Ethyl Acetate
EC	Electrical Conductivity
ESI	Electrospray Ionization
EU	European Union
FA	Formic Acid
Fenox	Fenoxaprop-p-ethyl
GC	Gas chromatography
IPM	Integrated Pest Management
IUPAC	International Union of Pure and Applied Chemistry
K_d	Solid/liquid partition coefficient

Koc	Soil Organic Carbon-Water Partitioning Coefficient
Kow	Octanol/Water Partition Coefficient
LC	Liquid Chromatography
LC50	Median Lethal Concentration
LC-MS/MS	Liquid Chromatography Tandem Mass Spectrometry
LD_{50}	Median Lethal Dose
LLE	Liquid-liquid extraction
LOD	Limit of Detection
LogP	Octanol-Water Partition Coefficient
LOQ	Limit of Quantification
LTP	Low temperature purification
ME	Matrix Effect
MeOH	Methanol
MRM	Multi Reaction Monitoring
MRLs	Maximum residue limits
MS	Mass spectroscopy
OC	Organic Carbon
OCPs	Organochlorine Pesticides
OP	Organophosphorus
POPs	Persistent Organic Pollutants
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
pK_a	Acid Dissociation Constant
PTFE	Polytetrafluoroethylene
Q1	Parent Ion
Q3	Fragment Ion
QuEChERS	Quick, Easy, Cheap, Effective, Rugged, and Safe
RCP4.5	Representative Concentration Pathway
RSD	Relative Standard Deviation
Rt	Retention time
SOM	Soil Organic Matter
SPME	Solid-phase microextraction
STEM	Science, technology, engineering, and mathematics
TCE	Trichloroethane

1. INTRODUCTION

The world population is estimated for the year of 2019 to be approximately 7.7 billion. This figure is expected to increase up to 8.5 billion by year 2030, and to 9.7 billion by the year 2050 (UN, 2019). As a result of this expeditious growth, global food demand and trading of agricultural products is crucial for the national economies (Kummu et al., 2020; Ongar, 2020). Consequently, increasing agricultural productivity by controlling crop pests and diseases has also gained tremendous emphasis in recent decades.

Although the first known pesticide application of protecting crops from damaging pests dates back to BC periods and takes its origin from the idea of defending human body from insects and parasites by applying elemental Sulfur dust by ancient Mesopotamians, the real change came into the stage with regards to the "Green Revolution" in the 1950s, which brought along a series of technological developments from the evolution of agrochemicals to the progress of new irrigation techniques and played a leading role in the development of modern agriculture (Hakeem et al., 2016; Tilman et al., 2002).

The U.S. Environmental Protection Agency (US EPA) describes pesticides as the materials that ensures the protection of agricultural products from noxious species (Moore et al., 2000; Ongar, 2020). Classification of the pesticides can be done in variety of ways. One of them is on the basis of mode of action and can be named as systemic and non-systemic pesticides. Systemic pesticides such as 2,4-dichlorophenoxyacetic acid exert their effect through direct absorption by plant tissues, while non-systemic pesticides show their effects by contact without entering the plant systems (Kumar et al., 2017). Another classification can be done according to the chemical compositions. The four main chemical groups of pesticides are; organochlorines (OCPs), organophosphates (OPs), carbamates, and pyrethroids (Figure 1.1.). OCPs contain at least five chlorine atoms in their structures and they are the first synthetic pest control agents that were used in the agricultural sector. On the other hand, OPs, as the name suggests, contain a phosphate group in their chemical structures. Carbamates are carbamic acid derivatives and pyrethroids are analogues of pyrethrins (Kumar et al., 2017). Pesticides can also be named by virtue of the pest which they are effective on. The most common examples that fit this description are; fungicides (effective against fungus), herbicides (effective against weeds), insecticides (effective against insects and arthropods), and rodenticides (effective against rodents) (Collotta et al., 2013). From another perspective and perhaps need to be more carefully considered,

these chemical substances can be characterized as endocrine disruptors that have a demolitive effect on the production of the hormonal cells (J. Zhang et al., 2016).

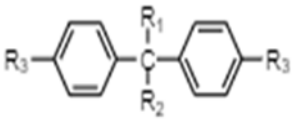
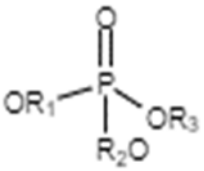
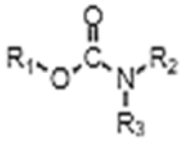
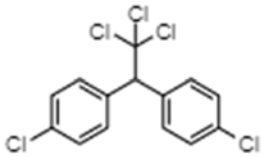
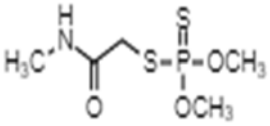
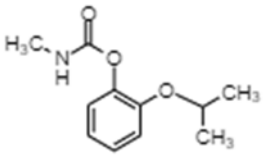
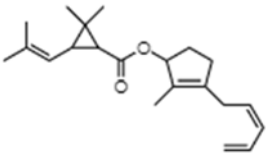
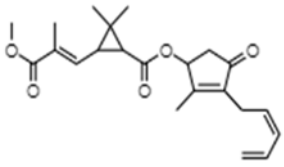
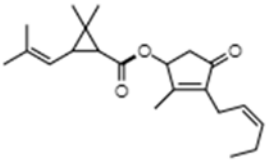
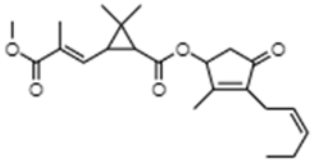
Organochlorines	**Organophosphates**	**Carbamates**
General Structure	*General Structure*	*General Structure*
		
Example	*Example*	*Example*
		
DDT	Dimethoate	Propoxur
	Pyrethrins	
		
Pyrethrin 1	*Pyrethrin 2*	*Jasmolin 1*
		
Jasmolin 2		

Figure 1.1. Chemical structures of main classes of pesticides (Kaushik & Kaushik, 2007; Georgiadis et al., 2018)

In the year 2019 roughly 2 million tons of pesticides have been applied and from the year of 2020 to present this number has increased up to approximately 3 million tones with an estimated budget of 50 billion USD. Among these two million tons of pesticides used, herbicides account for about half of this consumption (Akanksha Sharma et al., 2020; Anket Sharma et al., 2019). Figure 1.2 shows the global average use of pesticides per area of agricultural land. Figure 1.3 shows the average use of pesticides per area of croplands in Turkey (FAOSTAT, 2022). While there is a stable trend observed in pesticide use on a global scale since 2015, for the case of Turkey, there is a significant upward trend from the year of 2015 except the year 2018.

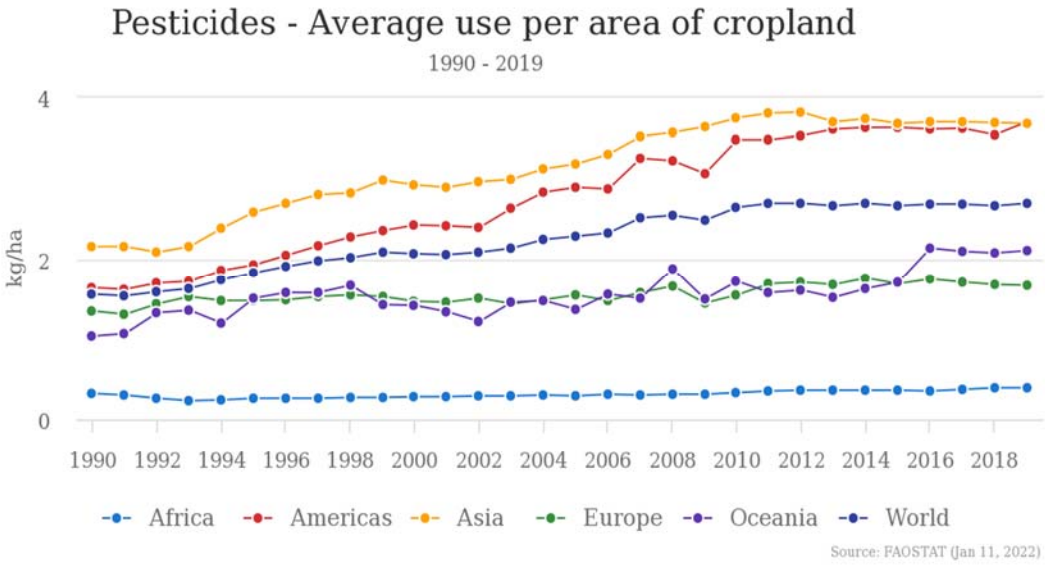


Figure 1.2. Global average use of pesticides per area of cropland (FAOSTAT, 2022).

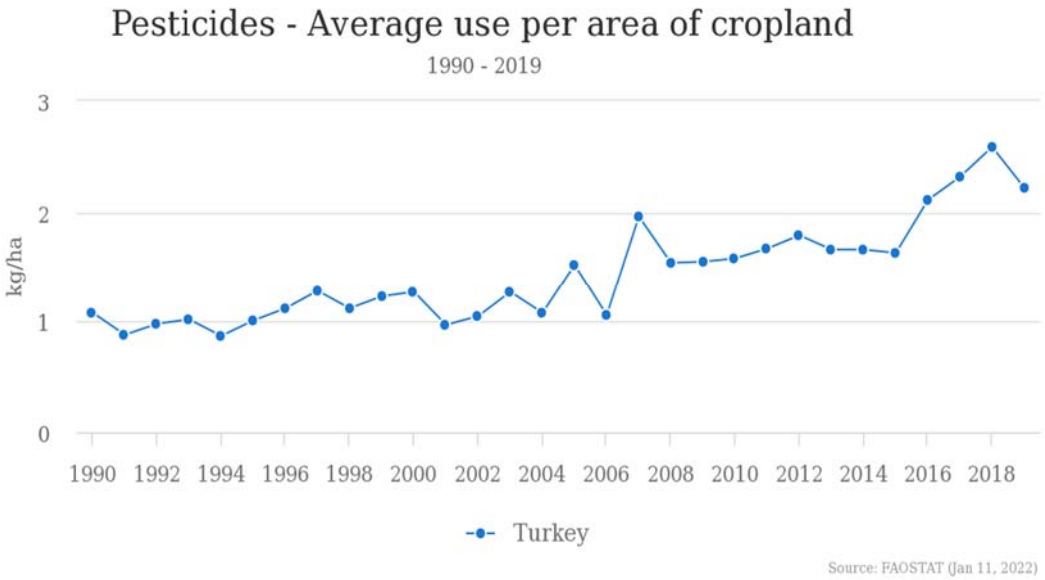


Figure 1.3. Average use of pesticides per area of cropland in Turkey (FAOSTAT, 2022).

By controlling pests and diseases, agrochemicals have been quite successful to the extent of meeting the growing demand for nutrition from the world societies. Elimination of the organisms that cause damage to the economy, increasing agricultural productivity, and preventing pathogenic vectors in living organisms are the areas where the use of pesticides is primarily favorable. Besides these benefits there are also secondary assets on the global and national economies, and society (Cooper & Dobson, 2007). However, many potential side effects of these agricultural chemicals have been revealed and supported by scientific data. In addition, by taking the enormous pesticide usage into consideration as it is mentioned before and in contemplation of enhanced understanding of the

effects of pesticides on natural systems and human health, it has been essential and a prerequisite to investigate the fate and transport behavior of these synthetic compounds in the environment. Stemming from the above- addressed issues and due to the gaps in the literature on the fate and transport mechanisms of this type of chemicals used in agricultural soils of Turkey, this study aims to interrogate the fate and transport potential of some commonly used herbicides by conducting batch and column experiments. The target herbicides are:

- 2,4-dichlorophenoxyacetic acid: It can be considered as a highly selective and a systematic herbicide mostly used for the control of undesired vegetation such as broad-leaved weeds. It is extensively applied to cereals, especially wheat which is widely grown in the Konya plain. The adverse effects include: irritation to the skin, severe damage to eyes and vision loss in advanced cases. It can be classified as moderately toxic to mammals and other livings. It is not considered to bioaccumulate. It is also can be classified as moderately toxic to birds, most aquatic species, some invertebrate and insects.

- Fenoxaprop-p-ethyl: It is classified as a post-emergence herbicide mostly used to control the unwanted growth of short-lived and long-lived grasses. Wheat, barley, turf and rice are the primary agricultural products that is aimed to be protected with this agrochemical. It can cause skin sensitization and due to its possible bioaccumulation pattern, it can cause some long-term unfavorable effects in the aquatic environmental systems.

Accordingly, 17 soil samples were collected from an agricultural company which is located in Karaman, Konya. These soil samples were processed for further experimentation in order to determine the fate and transport behavior of the selected chemicals. The samples were collected from the region of Konya which is one of the primary agricultural regions of Turkey.

2. LITERATURE REVIEW

2.1. A Granary of Central Anatolia: The Konya Basin

With an area of almost 5 million hectares, the Konya Basin is located in Central Anatolia, Turkey with a coordinate of 36.8° N 31.0° E and 39.5° N 35.1° E (Fig 2.1). Although there are sections in nine provinces an overwhelming part of the Basin is located in Konya (most of it is located in this province), Aksaray, Niğde and Karaman and a fraction of this terrain is floored by the arid Konya Plain (Waltham, 2015; WWF-Turkey, 2014). From the south, the Basin begins to be bordered by the Sultan Mountains, an extension of the Taurus Mountains, and from the north by the Pontic Mountains. The fact that it is surrounded by such high mountains gives the Konya Basin the characteristic of being a closed basin. Since it is a closed basin and is fed by many watersheds like Tuz Lake and Lake Beysehir, the Konya Plain has an important underground water reserve potential (Gokmen et al., 2012; Orhan et al., 2021).

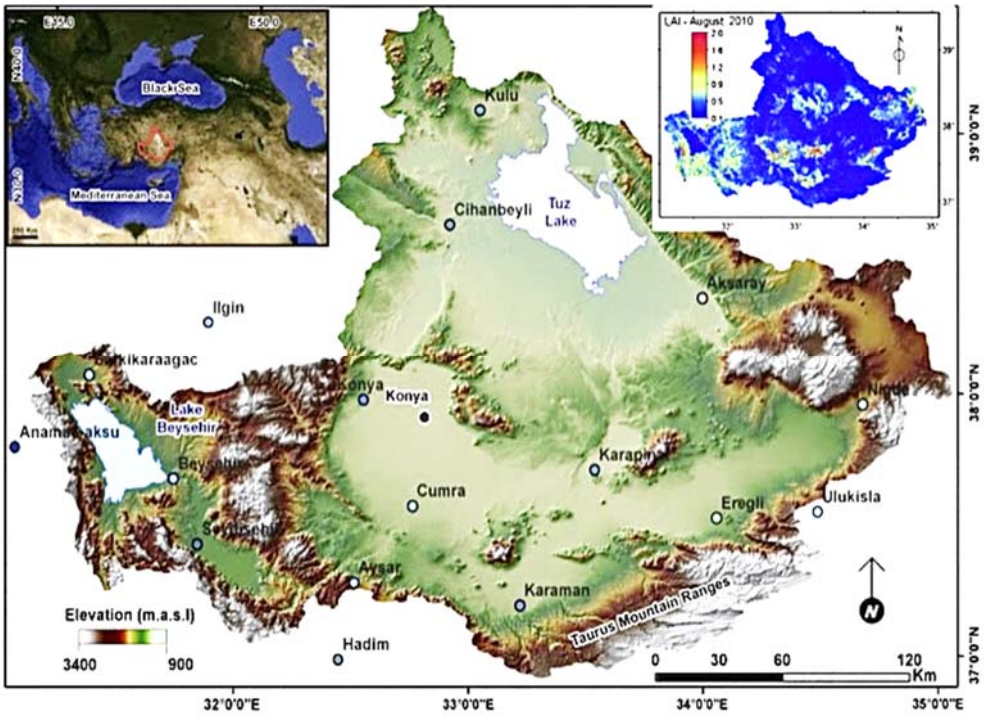


Figure 2.1. Physical and satellite view of the Konya Plain (Gokmen et al., 2012).

Konya plain is one of the driest regions in Turkey. The climate of the region is defined as semi-arid according to the Köppen classification and with warm-rainy winters and hot-dry summers, Mediterranean climate prevails in most of the parts of the plain (Güm & Kan, 2009). While the hottest

months are July and August, the lowest temperatures are recorded in January and February. Average annual temperatures range from -0.4°C to 23.0°C, which fluctuations characterize the continental climate of the basin (TÜBİTAK-MAM, 2010). As the long-term data indicates that the annual average rainfall amount in Turkey is roughly 600 mm, the precipitation pattern of the Konya Plain which varies between 280-350 mm, is significantly below the country statistics (T.C Çevre, Şehircilik ve İklim Bakanlığı, Meteoroloji Genel Müdürlüğü ;Topak and Acar 2006).

Table 2.1 shows the past, present, and estimated population of the four major cities in the region. With a rough appraisal presently 3 million people live in the Konya Plain and by the year 2040, with an increase of almost 2 million, it is anticipated that the number of individuals living in this region will approach 5 million. While the population increase rate in Turkey has dwindled in recent years and is classified as in the category of developing countries, the situation in the region reflects a similar trend. More than half of the people living in Karaman, Aksaray and Niğde city centers and at least 30% of people living in Konya city center are directly or indirectly dependent on agricultural production income. Since a rapid increase can be observed in the migration from rural to cities causing a decrease in the rural population, it is important to consider the population dynamics while making a regional development scenario (SYGM, 2015).

Table 2.1. Number of individuals living in the region based on years (SYGM, 2015)

	Population Based on Years				
CITY	**2015**	**2017**	**2019**	**2021**	**2023**
Aksaray	381.371	381.629	381.329	380.457	379.050
Karaman	237.881	239.298	240.512	241.549	242.350
Konya	2.092.117	2.116.077	2.137.894	2.157.659	2.175.214
Niğde	339.827	338.927	337.551	335.727	333.416
TOTAL	**3.051.196**	**3.075.931**	**3.097.286**	**3.115.392**	**3.130.030**

As it can be seen from Table 2.2, total land in four major cities in the Konya Plain cover up to 28.665.202 decares (1decare = 0.001 km^2) and this amount constitutes 12% of Turkey's total agricultural land (Figure 2.2)(SYGM, 2015). Konya Plain is an agricultural area where many types

of vegetables and fruits such as carrots, cherries and sour cherries are produced, as well as many field crops such as sugar beet, wheat, barley, dried beans, potatoes, sunflowers, poppy and corn. Stemming from this wide range of grain cultivation, the area can also be called a granary. Considering that the agriculture sector enables an immense employment potential in the region, with women comprising a majority of the labor force, it can be seen that the agricultural practices are at the origin of the economic activities in the Konya Plain (Kaygusuz, 2010).

Table 2.2. Agricultural Areas and Land Use in Turkey and the Konya Plain (2020) (SYGM, 2015).

CITY	**Total Land (km^2)**	**Cultivated Land (km^2)**	**Uncultivated Land (km^2)**
Aksaray	3.876	2.569	1.164
Karaman	3.270	2.626	171
Konya	18.763	14.603	3.316
Niğde	2.754	1.616	732
TOTAL	**28.665**	**21.415**	**5.384**
TURKEY	**230.949**	**153.873**	**33.873**

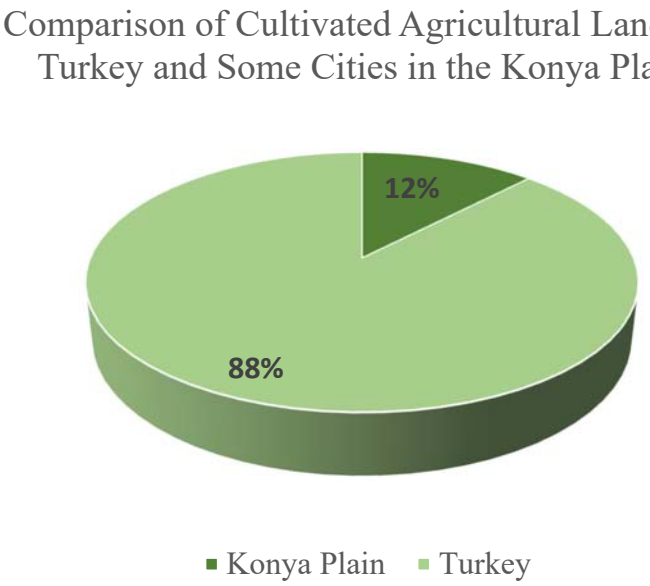


Figure 2.2. Comparison of Cultivated Agricultural Lands in Turkey and Some Cities in the Konya Plain (SYGM, 2015).

This intense agricultural activity in the region brings with it a lot of predicaments. Since Konya Plain is a semi-arid region and RCP4.5 scenario forecasts that the drought areas will be more prevailing in the forthcoming, water stress is one of these problems (Turkes et al., 2020). In the last half century, all the water resources were made available for indirect or direct agricultural use and led to alarmingly low water levels in natural wetlands (WWF-Turkey, 2014). Moreover, as a result of the strategy of enhancing the agricultural yield rather than improving environmental sustainability, the cultivation of products with high water needs such as alfalfa and sunflower has also become widespread (Yousefi et al., 2017; Huang et al., 2018). The support provided by the Ministry of Food, Agriculture and Livestock within the scope of the new legislations, in order to rapidly increase the sunflower cultivation areas in this area can be given as an example to this situation (WWF-Turkey, 2014). Due to the inadequacy of structural arrangements and regulations, many farmers still use highly water consuming irrigation methods such as furrow irrigation systems. In addition to these methods it is predicted that thousands of unlicensed wells are present illegally in the area (Lelandais, 2016).

Substantially, Konya plain is surrounded by plateaus mostly composed of limestone and as a karstic phenomenon this structure leads to natural sinkhole (obruk in Turkish)(Figure 2.3) formations but abnormal sinkhole formations emerge related with the illegal groundwater usage from the wells (Yaalon, 1972). These sinkholes, which can reach hundreds of meters in width, are also formed very close to the settlements, both threaten human life and make agriculture impossible , and their numbers are dramatically increased in years (Ozdemir, 2015; Orhan et al., 2021).

Another problem and the main focus of this thesis is the environmental pollution that is caused by agricultural activities. Ozcan and Aydin (2009) examined the levels of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in the urban air samples of Konya and they found out the concentrations of PAHs, PCBs and OCPs in the samples as 206 ng m−3, 0.106 ng m−3, 4.78 ng m−3 respectively. In addition to that, Yavuz et al. (2010) measured 24 OCP residues in 109 honey samples besides detectable levels of chlorinated pesticide residues and they reported that the most of the samples contained pesticide residues above the upper limits according to Turkish Alimentarius Codex (H. Yavuz et al., 2010). Another study showed that wheat samples taken from the Konya region were contaminated by OCP residues such as DDT, whose usage was banned decades ago (Guler et al., 2010).

Figure 2.3. Akviran Obruk, with a depth of 78 m and limestone walls (Waltham, 2015)

2.2. Hazards of Pesticide Usage

Agricultural chemicals have been highly successful increasing crop yields, crop quality, and saving both human and animal lives by reducing the harmful impact of invading species. However, among these benefits, due to their disadvantageous features such as bioaccumulation, long half-life, and wide range of contamination by dispersing through environmental systems, pesticide usage poses a risk to both human health and the environment. The possible risks, effects, toxicities and their entering routes will be discussed in this chapter.

2.2.1. Classification of Pesticides by Hazard

According to the World Health Organization (WHO), a hazard of a pest controlling agent can be characterized according to its acute risk it poses to overall health after a single or multiple short-term exposure. Hazard classification is mostly evaluated in two classes; more hazardous and less hazardous according to the toxicity of active ingredients and formulations. Solid state of pesticides can be considered less hazardous than liquid formulations due to flammable structure, easiness of dispersion, corrosivity etc.(WHO, 2009).

WHO also conducted experiments attempting to detect acute oral and dermal toxicity in the laboratory animals adhering fundamental toxicology assessment procedures mostly based on determination of median lethal dose (LD_{50}) (quantity of mg of toxic substance per kg weight of

laboratory animals that cause a destruction of half of their population)(WHO, 2009). Table 2.3 indicates the hazards of pesticides based on the acute oral and dermal toxicity to rats.

Table 2.3. Revised WHO hazard classification of pesticides (WHO, 2009).

		LD50 for the rat (mg/kg body weight) Oral		**Examples**	**Class**	**Reference**
Class		**Oral**	**Dermal**			
Ia	Exteremly hazardous	< 5	< 50	Dieldrin	Insecticide	(Yadav & Devi, 2017)
Ib	Highly hazardous	5-50	50-200	Carbofuran	Insecticide	(Arora et al., 2019)
II	Moderately hazardous	50-2000	200-2000	2,4-dichlorophenoxyacetic acid	Herbicide	(Ruiz de Arcaute et al., 2016)
III	Slightly hazardous	Over 2000		Fenoxaprop-P-ethyl	Herbicide	(Buckley et al., 2021)
U	Unlikely to present acute hazard	5000 or higher		DMST, Fludioxonil, Boscalid	Fungicide	(Taylor & Birkett, 2020)

For the assessment of toxicological levels in living organisms, some different approaches have been also developed. For instance, toxic levels in aquatic organisms can be established by using biomarkers (Echeverría-Sáenz et al., 2012). Barata et al., (2008) used Daphnia Magna (an aquatic invertebrate) feeding bioassay test as a worthwhile and responsive application for the determination of the toxicity levels in organochlorine pesticides contaminated water samples (Barata et al., 2008). Wilson et al., (2021) utilized from zebrafish embryos bioassay for the determination of pesticide contamination levels of four river basins located on the Pacific watershed of Panama and after an encounter with the river water samples and the embryos, they found out a substantial escalation in embryo mortality/abnormalities which is an indicator of high agrochemical pollution load in the rivers (Wilson et al., 2021). Moreover, seeds of L. sativum were subjected to a plant bioassay for the trans-chlordane toxicity establishment of activated sludge samples taken from Lund wastewater treatment plant, Lund, Sweden after a photochemical treatment. As a conclusion, by the help of the plant bioassay test, it was found that trans-chlordane was successfully deteriorated by the action of light through photolysis (Moradas et al., 2008).

2.2.2. Pesticides and the Environment

The wide use of pesticides poses a risk to all of the animal, plant and human life. Loss of biodiversity, loss of agricultural lands, contamination of groundwater resources and diminution of farmland bird population due to the decrease in the population of insects can be included in these risks (Echeverría-Sáenz et al., 2012). Once the pesticides are released to the environment even in small amounts, most of them can be found in various segments of the environment (Yadav & Devi, 2017).

When all the drawbacks of pesticide usage are taken into consideration, it gains importance to offer some regulatory amendments. Evaluation of the pests, regulation of pesticide application periods, prevention of crops from glaciation, interpretation of different classes of pesticide ingredients, and prevention of synergetic effects are the main pesticide resistance management strategies (H. Kaur & Garg, 2014). Besides these, Integrated Pest Management (IPM) approach can be considered as an eco-friendly implementation. The main target of IPM is to ensure to use greener chemicals instead of pesticides with toxic content. In more simple words, IPM is a new approach that consolidates all of the traditional methods in order to reduce the environmental side effects and to lower the economic inputs (H. Kaur & Garg, 2014).

2.2.3. Health Effects of Pesticides

It is estimated that agrochemicals are responsible for the death of 200,000 people annually worldwide (WHO, 2009). Even though the most common entering routes of pesticides to the human body are ingestion, inhalation or penetration through the skin (Figure 2.4), the major exposure is directly resulted from the consumption of pesticide contaminated nutrients (R. Kaur et al., 2019; Ongar, 2020). Since infants and youngsters are more adversely affected than adults when they uptake these toxic compounds to their bodies by nutrition, these age groups are extra vulnerable to the toxic effects that are resulted from the direct consumption of agrochemicals (Eskenazi et al., 1999). In addition to this, with over 1 billion laborers globally, another vulnerable group is people working in the agricultural sector. Factors such as direct exposure to the agrochemicals are of great importance in this risk classification (Curl et al., 2020).

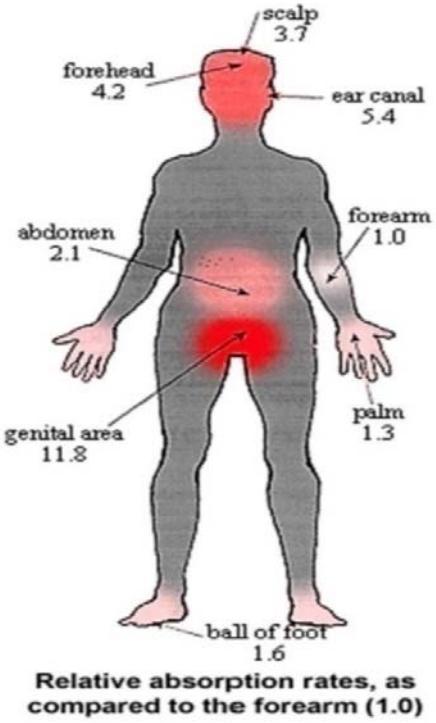


Figure 2.4. Absorption rates and entering routes of pesticides to human body (Kim et al., 2017)

The long-term side effects of pesticide exposure can be listed as; cancer, hormonal disorders, respiratory problems and due to the loss of the ability of motor and memory functions, neurodegenerative diseases such as Parkinson's and Alzheimer. On the other hand, the short-term side effects include, nausea, dizziness, abdominal pain, diarrhea, vomiting, headaches, and irritation of the nose, skin, eye, and throat (McCauley et al., 2006; ; Parrón et al., 2011; Allen & Levy, 2013; Collotta et al., 2013; Ongar, 2020). Freire & Koifman (2013) reviewed that there are strong links between the organophosphorus pesticide (OP) exposure and the increase of suicidal behavior, which is a serious health problem and one of the main cause of death among young individuals (Freire & Koifman, 2013). Moreover, Georgiadis et al., (2018) reported based on the literature of MEDLINE and Embase databases the higher risk of cardiovascular diseases caused by pesticide exposure related cardiotoxicity (Georgiadis et al., 2018). Other researchers have demonstrated a strong link between fertility and the pesticide exposure (Mehrpour et al., 2014). For instance, in a study conducted on 32 exposed and 25 non-exposed men farmers, Lerda & Rizzi (1991) have detected abnormal sperm functions in their semen due to 2,4-D exposure. Pesticide exposure level was measured from the urine samples and the mean value of 2,4-D concentration in the urine samples of exposed farmers was found at 9.02 mg L^{-1} (Lerda & Rizzi, 1991).

2.3. Pesticide Extraction Methods

Due to the complex and non-homogenous structure of the soil, it is highly challenging to determine the pesticide residues in soil at very low concentrations. In order to overcome this obstacle, some extraction methods are preferred to be used. Liquid-liquid extraction (LLE), solid-phase extraction (SPE), matrix solid-phase dispersion (MSPD), solid phase microextraction (SPME), and QuEChERS extraction are some of the examples of the extraction methods (Łozowicka et al., 2017). These methods will be briefly described in this section.

2.3.1. The QuEChERS Method

QuEChERS (quick, easy, cheap, effective, rugged, and safe) is a relatively new method for the extraction of pesticide residues from matrix samples such as soil and it consists of two main steps as salting-out with an extraction solvent and dispersive solid phase extraction (d-SPE)(Vera et al., 2014). The technique was firstly introduced by Anastassiades et al. (2003) by using single-phase extraction with acetonitrile (ACN) for the detection of agrochemical residues in high water content samples such as vegetables and fruits. Although there were limited applications for the pesticide residue extraction of soil samples, the first comprehensive study was conducted by Lesueur et al., (2008). In this study, the authors utilized a new ultra-sonication system for the extraction of commonly used pesticide residues from the soil matrix and compared the efficiency of the QuEChERS modified method with the other extraction methods. With the recoveries ranging from 27.3 to 120.9%, the QuEChERS extraction method was the most efficient one among the others (Lesueur et al., 2008).

Since the QuEChERS method was introduced to the service of the modern scientific world, it has attracted the attention of many researchers due to its simple, inexpensive, environment friendly and time-saving way of application rather than the traditional methods (Zhang et al., 2019). Other advantages of the method can be listed as low chemical usage, high precision, reduced errors, and enabling multi-residue analysis of the target contaminants (Zhang et al., 209). The QuEChERS method can be defined as a green chemistry approach due to aforementioned reasons (Pszczolinska & Michel, 2016).

According to the original QuEChERS method, 10 g of samples are transferred to centrifuge or Teflon tubes that are filled with ACN (1/1, v/w soil to water ratio), in addition to the first step soil-solvent mixture is mixed by shaking to initiate extraction, then anhydrous $MgSO_4$ and NaCl are added

in order to obtain a phase separation between water and the organic phases. Following these steps, an internal standard is added to the samples and the mixture is centrifuged. Finally, by the help of d-SPE approach as a clean-up step and an addition of a sorbent which is usually primary secondary amine (PSA), and an addition of anhydrous $MgSO_4$, recovery of ACN supernatant is achieved (Bruzzoniti et al., 2014). As a summary, addition of salts for the phase separation following the addition of the extraction solvent are the main steps for the original QuEChERS method.

In addition to the original method, two modified methods were introduced by the Association of Official Agricultural Chemists (AOAC) and by the European Standards (EN 15662). Briefly, while single-step acetate buffer is used for the AOAC QuEChERS extraction, citrate buffer is mostly preferred for the British Standard (AOAC, 2007; British Standard, 2008). Compared to the original method, the distinguishing part for these two modifications is the use of buffers.

In order to achieve higher extraction efficiencies, determination of the sample size is the most important step for both the original method and the modified ones when initiating the extraction procedure. Acetone, EtOAc and ACN are the solvents that are mostly used for the QuEChERS method. However, among these three, ACN is slightly more preferable due to its ability to extract pesticides that have different polarities (González-Curbelo et al., 2015). Lee et al. (2020) developed an analytical method for the detection of 85 persistent organic pollutant (POPs) multiresidues in human serum. In this study, they investigated the extraction efficiencies of different extraction solvents; EA, ACN, EA/ACN (1:1 v/v), hexane/acetone (1:1 v/v) and EA/hexane/acetone (1:1:2 v/v/v) respectively. They found out that ACN itself was successful in protein removal but its extraction efficiency decreased in the presence of chlorine and bromine atoms. Even though the accuracy was relatively low, the combination of EA/ACN showed the highest POPs recoveries in this study.

Salts are mostly used for the separation of aqueous phase (donor phase) from organic phase (acceptor phase) in liquid/liquid extraction (Kaufmann et al., 2014). The frequently used salts for the QuEChERS extraction can be listed as magnesium sulfate ($MgSO_4$), sodium chloride (NaCl), and sodium sulfate (Na_2SO_4). Due to its high dehydration capacity, $MgSO_4$ is said to be the most preferred salt to be used among the listed salting-out agents. Furthermore, $MgSO_4$ induces transfer of polar analytes from aqueous phase to organic phase by reducing the volume of the aqueous phase (C. Zhang et al., 2019). Wang et al. (2018) investigated the salting-out effects of $MgSO_4$ and NaCl on the extraction of the *Alternaria* toxins. It was observed that the 1:4 $MgSO_4$ to NaCl combination is the

best option for the salting-out step of the extraction as it is used in the original method (C. Wang et al., 2018).

2.3.2. Liquid-liquid extraction (LLE)

This extraction method is based on the solubility of the analytes in two different immiscible liquids, and it is also known as solvent extraction and partitioning. Liquid-liquid extraction (LLE) is not a mostly preferred extraction method since it is highly time- consuming, less-selective, and not environmentally friendly (Jin et al., 2012). Pirard et al. (2007) developed and validated a method for the multi-residue analysis of 17 different pesticides and some of its metabolites in honey samples using LLE and LC-MS/MS. For the LLE, diatomaceous earth was used as an auxiliary inert solid. Linearity was detected with a concentration range between 0.1 to 20 ng g^{-1} and with correlation coefficients ranging from 0.921 to 0.999. The study showed a robust, sensitive, reproducible and suitable method for the multi-residue analysis of the target chemicals (Pirard et al., 2007). In another study conducted on the honey samples, LLE was combined with low temperature purification (LTP) and the samples analyzed with gas chromatography (GC). Linear chromatographic response was detected with a concentration range between 0.033 to 1.7 μg g^{-1}, and with very low detection and quantification limits the method performance was efficient enough to analyze the target pesticides in 11 honey samples (de Pinho et al., 2010).

2.3.3. Solid-phase extraction (SPE)

Solid phase extraction (SPE) method provides a rapid purification and extraction of compounds in aqueous media and it is the most common method used for the pesticide extraction from the complex matrices such as soils. The working principle of the method is based on the affinity of the organic substances to a stationary phase such as alumina or silica gel (Dabrowska et al., 2003). Even though the SPE is more selective than LLE, being suspended of the some undesired impurities in the stationary phase besides the desired analytes is one of the drawbacks of this method (Buszewski & Szultka, 2012).

2.3.4. Solid-phase dispersion (MSPD)

Solid-phase dispersion aka matrix solid-phase dispersion is a mostly and efficiently used analytical method for the extraction, preparation and fractionation of the pharmaceutical, biological,

and viscous samples such as organ tissues (Barker, 2007; Jin et al., 2012). MSPD uses the fundamental principles of STEM (science, technology, engineering, and mathematics) for the extraction process. By mechanical blending of the samples with various sorbents, the technique allows a solvent-free extraction. Use of solid-support materials also enhances the efficiency of the blending process and ensures a complete disruption of the chemical structures (Barker, 2007). MSPD shortens the duration of the extraction, reduces the solvent consumption and the costs (Ramos et al., 2008).

2.3.5. Solid-phase microextraction (SPME)

The solid-phase microextraction (SPME) was firstly introduced at the end of 1980's and with no addition of excess solvents, the method had been quite successful for the analysis of large quantities of pollutants including agrochemicals. Like SPE, SPME is also a suitable pesticide extraction method from a liquid matrix. (Jin et al., 2012). For the detection of some organophosphorus pesticide residues in alcoholic and non-alcoholic beverages, Zambonin et al. (2004) developed a method by using SPME as an extraction method. GC/MS was used for the analysis of the target pesticides. While for the alcoholic beverage, limit of detection (LOD) and limit of quantification (LOQ) was detected as 2 to 33 ng ml^{-1} and 7 to 109 ng ml^{-1} respectively, this range was 2 to 90 ng ml^{-1} and 7 to 297 ng ml^{-1} for the non-alcoholic beverage samples which is below the maximum residue limits (MRLs) recommended by European legislations (Zambonin et al., 2004).

2.4. Fate and Transport of Pesticides in the Environment

The effectiveness of pesticides in controlling unwanted organisms has led to their widespread use and, consequently, to significant increase in crop yields in recent decades. As a result pesticides have been detected in groundwater, surface water bodies, the atmosphere and in regions far from their point of application, as far as the Arctic polar ice (Cheng, 1990). However, pesticides are noxious by nature, and many are persistent in the environment. The mobility and behavior mechanisms of pesticides through the soil and air until it disperses to different environments and the assessment of possible contamination risk as a result of this phenomena is an issue of global concern (Sarmah et al., 2004; Ongar, 2020). Transport processes can be described with these mechanisms: adsorption-desorption, volatilization, diffusion, runoff to water bodies, plant uptake, and leaching (Pateiro-Moure et al., 2013)(Figure 2.5). Soil water flow, pH, moisture content, temperature, volatilization, sodicity, and salinity are the main factors that affect the fate and transport of pesticides in the

environment. By resulting increases in global temperatures around the world, climate change also has an important effect on the issue by changing the aforementioned internal and external factors such as soil pH (Bloomfield et al., 2006; Ongar, 2020). In this chapter, the most common fate and transport mechanisms of the pesticides will be evaluated in detail.

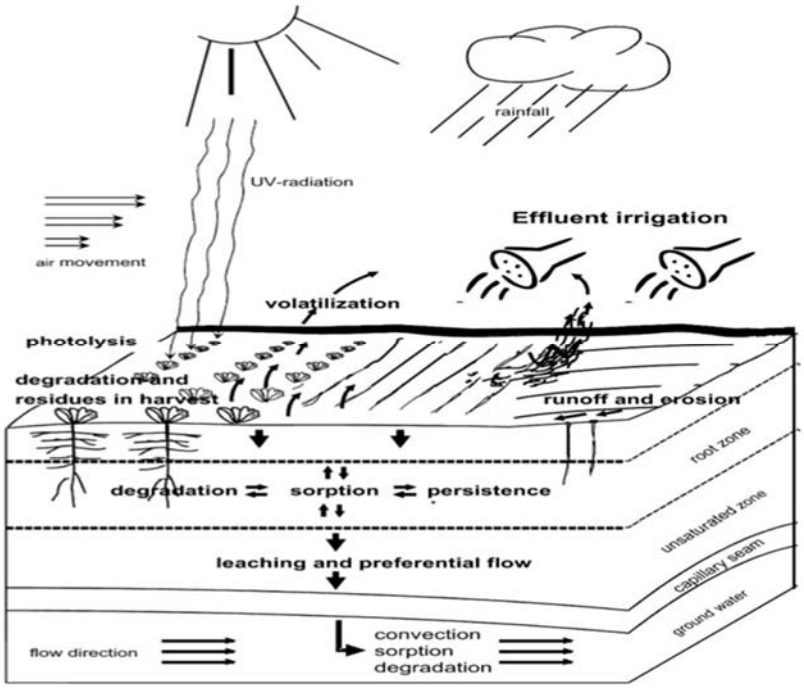


Figure 2.5. Schematic representation of fate and transport of pesticides in the environment (Müller et al., 2007)

2.4.1. Sorption

Soil sorption is one of the major fate and transport mechanisms of pesticides in the environment. The word sorption is used as a generic term for the description of adsorption-desorption processes and stands for any possible interaction with soil and soil-related environments (Odukkathil and Vasudevan, 2013). Chemicals can easily be sorbed onto the charged parts of the immobile structures such as soils and thus these chemicals are erroneously considered non-polluting to the water resources due to their immobilizations. Contaminants can also bind through the colloidal systems and can be transported by streams (McCarthy and Zachara, 1989). The sorption process directly affects the other fate and transport behaviors such as volatilization and degradation. Pesticide contamination levels in soils can be determined by investigating the sorption behavior by conducting both batch and column experiments and by analyzing the pesticide concentrations in the effluents with various analytical tools (Burke et al., 2013). Chemical and physical properties like molecular bonding, ion-exchange

capacity, soil organic percentage, pH, moisture content, and soil texture are the factors that play a key role in the sorption process (Müller et al., 2007).

The term adsorption is mostly governed by weak physical bonds between the atom or molecules such as van der Waals forces, or with more strong interactions by chemical bonds. In contrast, dissociation of adsorbate (contaminant in the bulk solution) from the adsorbent can be defined as the desorption process (Figure 2.6) (Ponnuchamy et al., 2021). In case of protracted contact of the sorbent with the adsorbate, it is expected the both adsorption and desorption tends to be at dynamic equilibrium which determines the maximum amount of adsorbate that is adsorbed by the adsorbent and is called as the adsorption capacity (Schuster, 1991; Ponnuchamy et al., 2021).

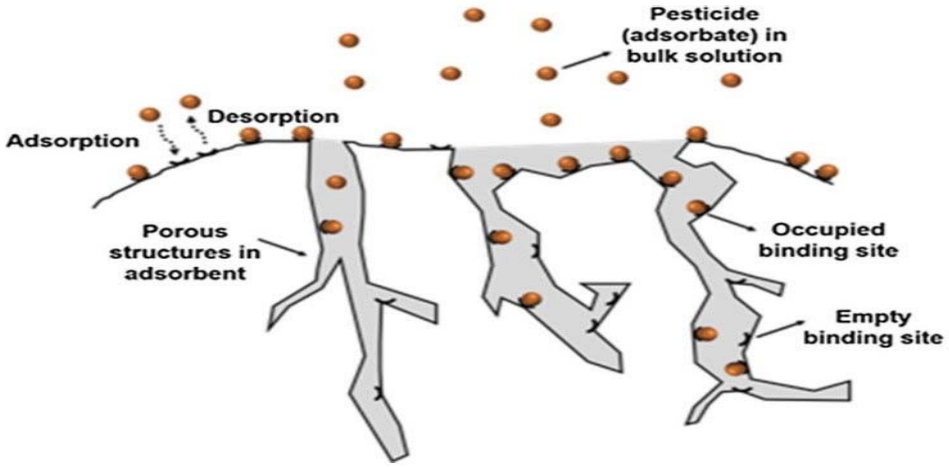


Figure 2.6. Illustration of the sorption process on the porous structure of the adsorbent (Ponnuchamy et al., 2021)

The most common sorption phenomenon is dominated by the weak physical interaction of non-polar or uncharged organic compounds on the hydrophobic sites of the soil organic matter (SOM). Stemming from this, chemical sorption affinity can be solely associated with the SOM (Karickhoff, 1981). Moreover, the distribution coefficient, K_d, can be calculated from the multiplication of the mass fraction of organic carbon in the soil f_{oc} (kg kg^{-1}) with the organic carbon partition coefficient K_{oc} (L kg^{-1}) (equation 2.1) (Limousin et al., 2007).

$$K_d = f_{oc} \times K_{oc} \tag{2.1}$$

In addition, the octanol/water partition coefficient, K_{ow}, is preferably used for the correlation of K_{oc} (L kg^{-1}) by establishing a logarithmic relationship (equation 2.2),

$$\log(K_{oc}) = n\log(K_{ow}) + k \quad (2.2)$$

Where n and k are the constants mostly dependent on the SOM and the chemical properties of the organic adsorbent. Since these constants tend to remain perpetual for a broad spectrum of soils and organic adsorbents, it gives a chance of proper estimation of the adsorption process of uncharged organic chemicals even at very low concentrations by using the K_{oc} and K_{ow} (Limousin et al., 2007).

2.4.1.1. Pesticide Partitioning in Soil. Pesticides in soil are mainly present in three phases (liquid, gas, adsorbed) and these phases are commonly at equilibrium. In order to establish the equilibrium concentrations of the phases, calculation of partition coefficients is a necessity. For this purpose, the Henry's Law constant (K_H) can be used for the interpretation of the partition coefficient between the gas and liquid phases (Equation 2.3)(Koziol and Pudykiewicz, 2001).

$$K_H = \frac{C_G}{C_L} \quad (2.3)$$

While C_L stands for the concentration (kg m^{-3}) of the substance in a liquid phase, C_G stands for the concentration (kg m^{-3}) of the same substance in a gaseous phase (Koziol and Pudykiewicz, 2001).

2.4.1.2. Soil Sorption Isotherm Models. The relationship between the sorbed concentration and the aqueous phase concentrations at equilibrium can be shown linearly by a straight line (Equation 2.4) (Karickhoff, 1981).

$$C_S = K_D \times C_W \quad (2.4)$$

In this equation while C_S represents the sorbed concentration (kg kg^{-1}) of a substance, K_D (m^3 kg^{-1}) represents the slope of the linear sorption isotherms and C_W is the aqueous concentration (kg m^{-3}). In addition to linear sorption isotherm, non-linear sorption isotherms are widely used in the literature such as Freundlich (Equation 2.5) and Langmuir (Equation 2.6) models (Müller et al., 2007).

$$C_S = K_f \times C^n \quad (2.5)$$

Where C corresponds to the equilibrium concentration of a substance in aqueous phase (mmol L^{-1}), C_s indicates sorbed concentration of a substance (mmol kg^{-1}), K_f and n are Freundlich coefficients.

$$C_S = \frac{k \times b \times C}{1 + kC} \quad (2.6)$$

Where k and b are empirical parameters. The main difference between the Freundlich and Langmuir models is that the Langmuir isotherm model represents a finite number of binding sites and thus it can indicate the maximum level of adsorption (Sarmah et al., 2004).

2.4.2. Volatilization

Pesticide airborne movement as a gaseous state from soil, herbs, and water sources such as aquifers is described as the volatilization process of pesticides. This gaseous state movement can also be named as "drift". In their gaseous forms, these agrochemicals are spread over a wider area than their initial targets and can cause detrimental damage to human and other living conditions (Gao et al., 2012). Once a pesticide enters the atmospheric cycle, there are many factors that can affect the transport of these chemicals. Although climatic conditions among these factors, there is still limited information about how the climatic factors such as seasonal precipitation affects the transport process (Galon et al., 2021).

2.4.3. Degradation

Pesticides are highly persistent in natural environments and even in very low quantities, pesticide residues are omnipresent in environmental systems. Investigation of the degradation behavior of agrochemicals gains importance due to this ubiquitous existence. Degradation of the pesticides in the environment occurs both abiotically and biotically. While the biotic processes are mostly carried out by microorganisms or plants, photo and chemo transformation contributes to the degradation mechanism of the abiotic processes (Müller et al., 2007; Fenner et al., 2013).

2.4.3.1. Biotic degradation. Existence of microbial community is the most substantial cause of pesticide biotic degradation. While bacteria utilizes energy and nutrients from pesticides by metabolizing them, on the other hand, in case of intake of pesticides, eukaryotes randomly metabolize and transform pesticide ingredients via their broad range of enzymes (Walker et al., 2001; Fenner et al., 2013). Biotic degradation rate is dependent on some of the soil characteristics such as pH, organic

and ionic content. Frequency of the pesticide application also affects the biotic degradation rate (Walker et al., 2001). In a study on Dufulin (herbicide) degradation, Wang et al. (2014) established that the type of the soils have a significant impact on biotic degradation of Dufulin with approximate half-life differences up to twice. In addition, they have found that the degradation rates were decreased in the sterilized soil samples which is an indicator that Dufulin was degraded successfully by the biotic environment (Wang et al., 2014).

2.4.3.2. Abiotic degradation. Abiotic degradation involves photochemical transformations and chemical reactions such as hydrolysis, photolysis, elimination and oxidation-reduction reactions. Since pesticide application mostly occurs outdoors, direct contact of these chemicals with sunlight is unavoidable and leads to photolysis. Photolysis is accelerated in the presence of high organic content and fine soil texture (Müller et al., 2007). Moreover, pesticide degradation by the help of using a semiconductor is a promising and a relatively new method for the scientists especially for the elimination of the pesticides in the wastewater treatment process. The working principle of this method is based on the transformation of toxic substances into photosynthesis reactants and inorganic salts. Different kinds of metal oxide semiconductors can be used for this process (Vaya & Surolia, 2020).

2.4.4. Leaching

Due to the complex and heterogenous nature of the soil, it is difficult to predict the leaching behavior of the chemical substances. For this reason, the soil is investigated under the two headings as: soil composition and soil profile. Soil profile can be identified as the integrity of the vertical sections (horizons) of soil. From top to bottom, soil horizons are divided as O, A, B, C, and R, (Figure 2.7.) respectively. On the other hand, the term soil composition is mostly used to describe the inorganic and organic content of the soil (Pérez-Lucas et al., 2019). Plantation occurs usually at the horizon O and it can be named as an organic layer. The horizon A is the surface soil and besides the organic matter, most of the micro and micro nutrients are abundant at this level. As a subsoil level, horizon B has a lower organic content than horizon A and it takes its coloration from iron oxides. The A and B horizons precisely overlie the solid rock. The horizon C aka substratum, is the layer where $CaCO_3$ accumulation takes place. The bottom layer R cannot be classified as soil but it is the hard bedrock (Nature, 1961).

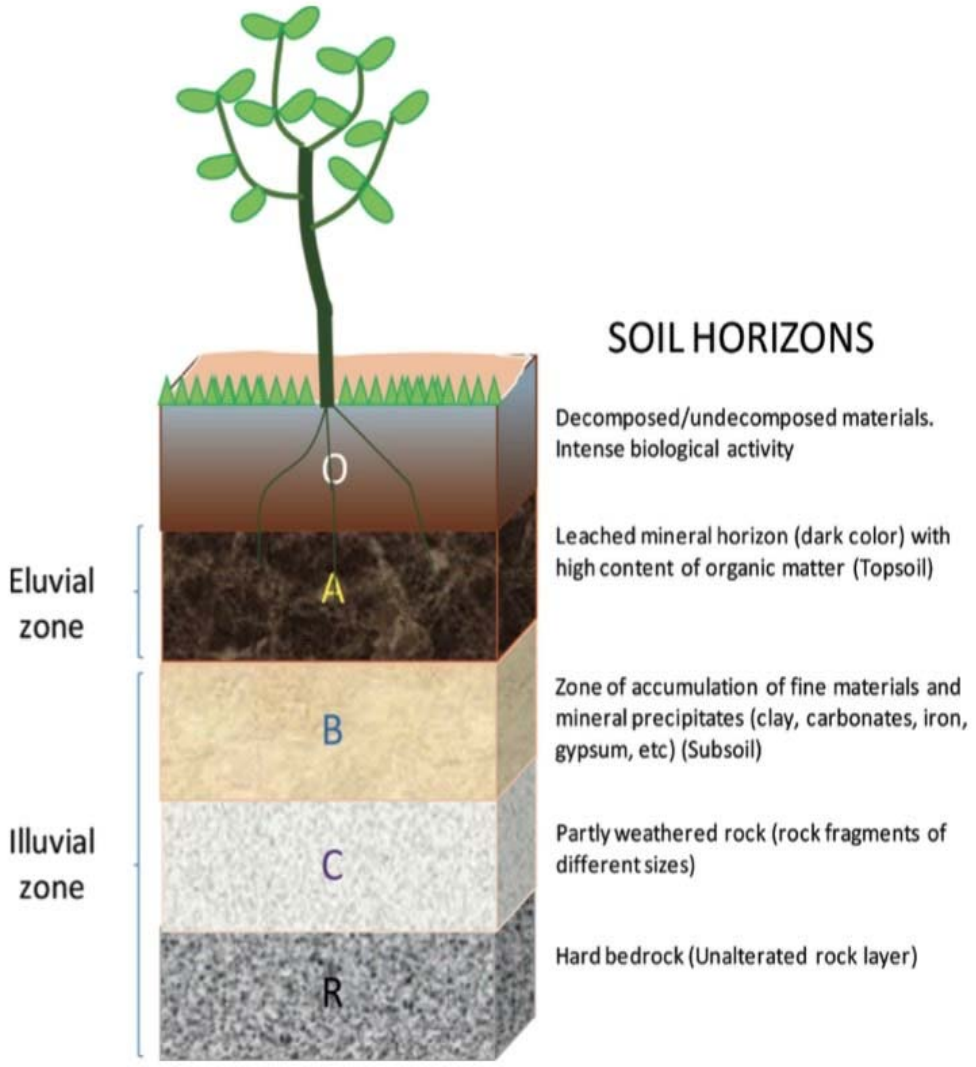


Figure 2.7. Soil horizons (Pérez-Lucas et al., 2019)

Pesticide leaching can be described as the downward movement of agrochemicals from the ground surface through the unsaturated soil zone until they reach groundwater resources (Steffens et al., 2013). Most of the climatic factors have an impact on pesticide leaching through the soil but the major component that enables this downward movement is the precipitation pattern. In areas with heavy rainfall, it is evident the pesticide leaching frequently on the upbeat (Steffens et al., 2013).

The other factors that affect the leaching are sorption, soil characteristics, degradation, and climatic conditions respectively. In addition, the leaching process can be examined usually by repacked soil columns. The main principle relies on change of the concentration of the target pesticide in the effluent when an artificial percolation is achieved (Müller et al., 2007).

2.4.4.1. Pesticide Transport at Equilibrium. Understanding the relation between the water flow and the pesticide movement through the homogenous soil by the common equations (Richard's equation for the water movement and solute transport equation) is important for agricultural practices. Equation 2.7 describes the transport, sorption, and uniform advective transport at equilibrium conditions (Jury & Flühler, 1992).

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} \tag{2.7}$$

Where, C represents the pesticide concentration (M L^{-3}), D indicates the hydrodynamic dispersion coefficient (L^2 T^{-1}), v is the average pore-velocity (L T^{-1}) and z is the length (L). On the other hand, the retardation factor (R) is shown in Equation 2.8, where θ is the volumetric water content (cm^3 cm^{-3}) and ρ_b is the soil bulk density (g cm^{-3}) (Jury & Flühler, 1992).

$$R = 1 + \frac{\rho_b K_d}{\theta} \tag{2.8}$$

2.4.5. Laboratory Studies: Batch and Column Experiments

Since the fate and transport of pesticides is an important phenomenon in understanding of contamination of the environmental systems, it is essential to estimate the sorption and leaching behaviors of these chemicals. With this reason, batch and column experimental setups are commonly used together for a more detailed examination of the mobility of pesticides through the environment.

The underlying principle of the soil batch sorption experiments is contacting known amount of soil with a solution that contains definite concentration of adsorbent and then measuring the final concentration of the target substance at the effluent after reaching the equilibrium conditions (Limousin et al., 2007). The batch tests are preferred to be used for the estimation of the sorption behavior of the chemical substances such as pesticides due to its easiness of application. However, column sorption tests are considered to give more reliable data since the batch method requires inconvenient solid/solution ratios and its success is controversial in porous media (Burke et al., 2013). Benker et al. (1998) compared the calculated retardation coefficients of trichloroethane (TCE) both from the batch and column experiments. Results showed that even though batch experiments were successful for the determination of the retardation coefficients, they are not as effective as the column experiments for the estimation of TCE mobility with regards to the sorption of the target contaminant

by the type of the material (teflon-coated silicone liner) that is used for the preparation of the batches (Benker et al., 1998).

The column sorption tests are also used for the estimation of distribution coefficient, Kd, values and for the monitoring of contaminant transport by applying artificial water application through a column that is filled by geological structures but in a better way of simulation of the environmental conditions rather than batch sorption tests (T. H. Wang et al., 2009). The sizes of the soil columns can be in a very wide range: from milliliters to meters in diameter and from grams to tonnes by mass (Lewis & Sjöstrom, 2010).

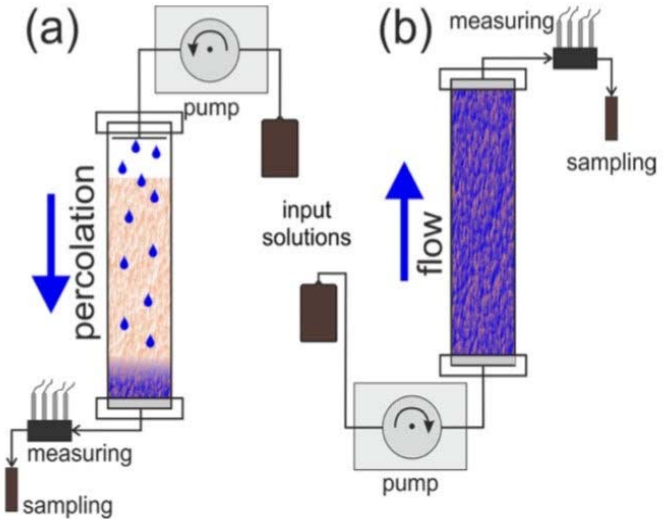


Figure 2.8. Schematic presentation of the workflow of a column experimental setup: a) an unsaturated column, and b) a saturated column (Banzhaf & Hebig, 2016)

Soil columns can be classified in two ways: according to the saturation situation, or according to the way of construction. When a column is filled by liquid or Dense Non-Aqueous Phase Liquids (DNAPL) until there are no air gaps left in their pores, it is called saturated columns. In contrast, unsaturated columns operated in the presence of air in the soil pores. (Aminnaji et al., 2021; Lewis & Sjöstrom, 2010). Two main classifications based on the construction have been evaluated: packed (disturbed) columns and monolithic (undisturbed) columns. While air-dried and meshed soil samples are usually used as a compaction material in the packed columns, monolithic columns use undisturbed soil in order to stimulate the natural conditions in the best way possible (Lewis & Sjöstrom, 2010).

Homogenous structure of the bulk densities in the packed columns enables a reproducibility. The soil bulk density can influence the transport mechanisms of the column and it can be calculated by

dividing the total mass of soil to the volume of the column that is occupied by the soil. The relation between the amount of the compacted soil and the porosity can be expressed in the Equation 2.9 (Lewis & Sjöstrom, 2010).

$$n = \frac{\rho_b}{\rho_s} \tag{2.9}$$

Where, the particle mass density is shown by ρ_s (air-dried mass divided by the volume of the soil) and ρ_b indicates the bulk density (Lewis & Sjöstrom, 2010).

Even though the column sorption tests are quite effective for the fate and transport studies, there are some drawbacks. For instance, the experiments can be highly time consuming especially when the columns are filled by clayish soils that have low hydraulic conductivity (Limousin et al., 2007). However, the main disadvantage involves any kind of interaction of the target chemical with the experimental environment. In order to simplify and to understand the hydrodynamic properties of the column, a nonreactive tracer such as Cl^- and Br^- is used (Limousin et al., 2007).

2.5. Pesticide Residue Analysis with LC-MS/MS

Pesticide residues can be found at very low concentrations in complex matrices, from adipose tissues to food chain, and their detection entails the use of sensitive and selective analytical tools and methods. At this point, coupling the liquid chromatography (LC) with the mass spectroscopy (MS) can be thought of as a highly selective analytical technique for the determination of the pesticide residues in a wide range of samples (Núñez et al., 2005).

In the LC-MS systems, the target compounds are physically separated in a specific time of interval in LC, and then generated ions formed by an ionization source are further separated in the mass analyzer part of an MS system based on their mass-to charge ratios (m/z) (Kruve et al., 2015). For an advanced sensitivity and selectivity, tandem mass spectrometers (MS-MS) can be used firstly by generating a precursor ion in the first quadrupole, and then after the collision, by forming the product ions in the third quadrupole (Zhou et al., 2006).

Selection of the mobile phase and the type of the column has a paramount importance when evaluating the performance of the LC. While, C8 and the C18 types are preferred to be used as columns; as an aqueous phase pure water, and as an organic phase methanol are commonly used as

mobile phases (Kmellár et al., 2011). Also in order to increase the efficiency of the procedure, some additives and buffers such as phosphate, borate, formic acid and ammonium formate are used (Kmellár et al., 2011).

Since the LC and MS systems are substantially incompatible, there arose a need for a connection of the devices with an interface. As atmospheric pressure-ionization (API) strategies; electrospray ionization (ESI), atmospheric-pressure chemical ionization (APCI), and atmospheric pressure photo-ionization (APPI) can be given examples of some of the major interfaces of the LC-MS system (Zhou et al., 2006). Although the API sources are quite effective in the highly precise determination of the target compounds, one of the main drawback is the inability to do the analysis of a wide range of samples in a single run, hence, a multi-residue method (MRM) should be developed for the analysis of a large number of compounds (Fernández-Alba & García-Reyes, 2008).

Triple-quadrupole and ion-trap are the most common mass analyzers of the MS/MS systems (Núñez et al., 2005). For instance, besides the high sensitivity and well quantitation, triple-quadrupole (QqQ) is capable of simultaneously monitoring multiple transitions (Kmellár et al., 2011). In addition, triple-quadrupole analyzers are more sensitive than the ion-trap analyzers. On the other hand, ion-trap analyzers are useful at multi-stage fragmentation and can be used for the screening purposes (Núñez et al., 2005).

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Chemical Substances

All the target herbicides (2,4-D and Fenox) and surrogate standards were purchased at their purest grade from Sigma Aldrich Chemicals Company for the development of the analytical method and for the quantification of these chemicals in the soil samples. The detailed information about chemical structures, molecular weight, and etc. of both the target herbicides and surrogate standards is given in Table 3.1 and Table 3.2 respectively.

Table 3.1. Structure, molecular weight, abbreviation, CAS# and the LC-MS/MS ionization of the target herbicides

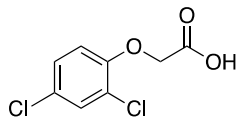
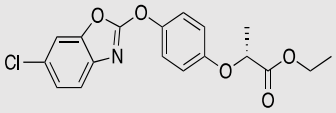
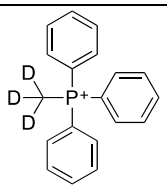
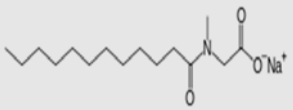
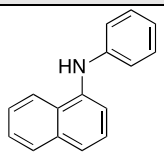
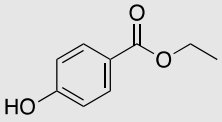
Herbicide	**Abbreviation**	**Cas No.**	**Molecular Structure**	**Molecular Weight (g mol^{-1})**	**LC-MS/MS Ionization**
2,4-dichlorophenoxyacetic acid	**2,4-D**	94-75-7		221.04	Negative
Fenoxaprop-p-ethyl	**Fenox**	71283-80-2		361.78	Positive

Table 3.2. Structure, molecular weight, abbreviation, CAS# and the LC-MS/MS ionization of the surrogate standards used for QA/QC of the analysis

Surrogate Standard	**Abbreviation**	**Cas No.**	**Molecular Structure**	**Molecular Weight (g mol^{-1})**	**LC-MS/MS Ionization**
Methyl-d3-triphenylphosphonium	**Pos 1**	1560-56-1		407.2	Positive
Sodium (N-methyldodecanamido) acetate	**Neg 1**	137-16-6		293.38	Negative
N-phenyl-1-naphthylamine	**Pos 2**	90-30-2		219.28	Positive
Ethyl paraben	**Neg 2**	120-47-8		166.17	Negative

Stock solutions of the listed chemicals were individually prepared at 10 or 1 g/L in methanol and stored at -20ºC in 10-mL amber vials until use. A composite working solution of analytes and the internal standards was prepared at 100 mg L^{-1} each by adding 100 µL of IS's and 2,4-D and 1 mL of Fenox and MSM in 10 mL MeOH.

Chemicals used in the characterization of the soil samples, QuEChERS extraction and LC-MS/MS analysis are listed in Tables 3.3 and 3.4 respectively.

Table 3.3. Chemicals used in the characterization of the soil samples

Chemical	**Chemical Formula**	**Molecular Weight (g mol^{-1})**	**CAS No.**	**Area of Use**
Potassium chloride	KCl	74.56	7447-40-7	pH
Hexaamminecobalt(III)chloride	$H_{18}N_6Cl_3Co$	267.48	10534-89-1	EC
Acetic acid (glacial)	$C_2H_4O_2$	60.02	64-19-7	CEC
Ammonium hydroxide	NH_4OH	35.05	1336-21-6	CEC
Isopropyl alcohol	C_3H_8O	60.10	67-63-0	CEC
Sodium acetate trihydrate	$CH_3COONa.3H_2O$	136.08	6131-90-4	CEC

Table 3.4. Chemicals used in the QuEChERS extraction and LC-MS/MS analysis

Chemical	Chemical Formula	Molecular Weight (g mol^{-1})	CAS No.	Area of Use
QuEChERS				
Acetonitrile	C_2H_3N	41.05	75-05-8	Extraction
Acetic acid (glacial)	$C_2H_4O_2$	60.02	64-19-7	Extraction
Deionized water	H_2O	18.06	-	Hydration
Magnesium sulfate	$MgSO_4$	120.37 (anhydrous)	7487-88-9 (anhydrous)	Salting-out
Sodium Acetate	$C_2H_3NaO_2$	82.03	127-09-3	pH adjustment
Sodium Chloride	NaCl	58.44	7647-14-5	Salting-out
LC-MS/MS analysis				
Methanol	CH_3OH	32.04	67-56-1	Mobile phase
HPLC grade water	H_2O	18.02	7732-18-5	Mobile phase
Formic acid	HCOOH	46.03	64-18-6	Mobile phase

3.1.2. Soil Samples

Before conducting the experiments, a commercial plant soil was purchased in order to be used as a blank soil sample for method optimization studies of extraction, batch and column experiments.

All of the soil samples that were used in the experiments were collected from a field located in Karaman, near the district of Karapınar, Konya. The field is actively operating a focus on animal husbandry and farming. Their agricultural production mostly consists of crops such as wheat, barley, sunflower, corn, and fruits such as apple and almond. Irrigation activities of the farm were carried out with a “Drip Irrigation System”. The farm uses a wide range of pesticides similar to the pesticides used in the entire Konya Plain.

For the extraction, batch and column experiments a total of 17 soil samples (from depths of about 10 to 20 cm) were collected on March 25, 2021 from five different fields: (i) wheat, (ii) rotation of wheat/corn, (iii) barley, (iv) apple and (v) uncultivated land (background). Detailed information about soil sampling sites is listed in Table 3.5. Soil samples weighing approximately 1.5-2 kg each were

placed in zip-lock bags and shipped to the laboratory of the Institute of Environmental Sciences, Boğaziçi University, immediately after sampling.

Table 3.5. Information about the soil sampling sites.

Location	Crop	Herbicide Applied	Remarks
Pivot 2	Wheat	Kalson, Resital duo, last application: May 23, 2020	Crop rotation, previously corn
Pivot 2	Wheat	Kalson, Resital duo, last application: May 23, 2020	Crop rotation, previously corn
Pivot 2	Wheat	Kalson, Resital duo, last application: May 23, 2020	Crop rotation, previously corn
Pivot 2	Wheat	Kalson, Resital duo, last application: May 23, 2020	Metal form, surface soil
Pivot 2	Wheat	Kalson, Resital duo, last application: May 23, 2020	Metal form, surface soil
Pivot 7	Wheat	Topik, Granstar, last application: April 7, 2020	_
Pivot 7	Wheat	Topik, Granstar, last application: April 7, 2020	_
Pivot 7	Wheat	Topik, Granstar, last application: April 7, 2020	_
Pivot 8	Apple	_	Below tree
Pivot 8	Apple	_	In gap between tree rows
Pivot 8	Apple	_	Below tree
Near enterance (Uncultivated)	Uncultivated	_	Has not been cultivated since the opening of the farm
Near enterance (Uncultivated)	Uncultivated	_	Has not been cultivated since the opening of the farm
Near enterance (Uncultivated)	Uncultivated	_	Has not been cultivated since the opening of the farm
Pivot 13	Currently uncultivated, last year barley	Foxtrot, Granstar, last application: March 25, 2020	Corn will be planted later this year (fallow)
Pivot 13	Currently uncultivated, last year barley	Foxtrot, Granstar, last application: March 25, 2020	Corn will be planted later this year (fallow)
Pivot 13	Currently uncultivated, last year barley	Foxtrot, Granstar, last application: March 25, 2020	Corn will be planted later this year(fallow)

3.2. Methods

3.2.1. Soil Sampling

In order to avoid contamination, mislabeling and misplacing, special care was taken by collecting the soil samples according to standard procedures. Before the sampling, sampling sites and the number of the samples were determined. Predetermined soil samples were collected from depths of approximately 10 to 20 cm (Figure 3.1). 1-1.5 kg of each sample was transferred into clean and labeled zip-lock bags and delivered to the laboratory of the Institute of Environmental Sciences, Boğaziçi University for detailed soil testing.

In order not to disturb soil microbial population and the chemical content, the soil samples were air dried at room temperature in plastic containers before any further experimentation. The soil samples were grinded and sieved through 2-mm mesh as it is described in internationally recognized ASTM standards after the drying process (ASTM, 2017). After all, air-dried soil samples were placed in zip-lock bags and stored at +4ºC.

Figure 3.1. A soil sampling zone

3.2.2. Characterization of Soil Samples

3.2.2.1. Soil Moisture. In order to determine the soil moisture, the collected soil samples (100 g each) were transferred into a plastic container with a perforated lid and let them air-dry at room temperature (Figure 3.2). The drying process, which was 18 days, was continued until sample weight stabilized the weight reduction was controlled at intervals of 2 days.

Figure 3.2. Air-drying process of soil samples in plastic containers

3.2.2.2. Total and Volatile Solids. To determine the total and volatile solids of the soil samples, standard Method 1684 of U.S. Environmental Protection Agency (U.S. EPA)(Telliard, 2001) was followed. Soil samples of a known weight were evaporated to a constant weight condition for 24 hours in an oven maintained at a temperature of 105 °C (Equation 3.1, 3.2). The mass of the remaining part was monitored. After the determination of the total solids, the dried sample was cooled at room temperature, weighed, and ignited in a muffle furnace at 550 ° C to get rid of volatile solids present in the sample (Equation 3.3).

$$\%\text{Moisture} = \left(\frac{\text{A}}{\text{B}}\right) \times 100 \quad (3.1)$$

$$\%\text{Total solids} = \left(\frac{C}{B}\right) \times 100 \quad (3.2)$$

$$\%\text{Volatile solids} = \left(\frac{D}{C}\right) \times 100 \quad (3.3)$$

A=(Weight wet sample+crucible) - (Weight dry sample+crucible) (g)

B=((Weight wet sample+crucible) - (Weight empty crucible) (g)

C= (Weight dry sample+crucible) - (Weight empty crucible) (g)

D= (Weight dry sample+crucible) - (Weight of residue and dish after ignition) (g)

3.2.2.3. pH. For the pH measurements the standard method of Food and Agriculture Organization of the United Nations (FAO) was followed (FAO, 2011). Firstly, in order to prepare a 250-mL 1.0 M KCl solution 18.64 g of KCl was dissolved in approximately 200-mL of DI water and then the volume was made up to 250-mL. Air-dried and sieved soil samples (2.5 g) were mixed with 12.5 mL 1.0 M KCl solution (with a soil to 1.0 M KCl ratio 1:5, w/v) in 50-mL centrifuge tubes and mixed for homogenization. Then the mixture was let stand for 60 min. The pH values were measured by pH meter from the unstirred supernatant.

3.2.2.4. Sieve Analysis. The Endecotts EFL 2000 vibrating shaker was used for the sieve analysis of the samples. With the widest aperture at the top, eight sieves with mesh numbers 4, 10, 20, 40, 70, 100, 140, and 200 were stacked up (Figure 3.3.). The sieve stack was placed on top of the receiver. Then the soil samples (200 g) were transferred to the top sieve, the lid was fitted and the process was started.

a) b)

Figure 3.3. a) Endecotts EFL 2000 vibrating shaker with the mesh stack on it b) Mesh with soil sample

3.2.2.5. Soluble and Exchangeable Cations. For the determination of soluble and exchangeable cations (Na^+, Ca^{2+}, Mg^{2+} and K^+) the standard method of British Standards Institution (2018) was followed (BS EN ISO, 11260). Firstly, by dissolving 4.46 g of hexamminecobalt(III)chloride in a 1-L volumetric flask containing 700 mL of DI water and made up volume, 0.016 mol/L hexamminecobalt(III)chloride solution was prepared. 1 g of fine-ground calcite was added to the solution and the mixture was placed in an ultrasonic bath for 30 min. The solution was mixed by using a magnetic stirrer for about 30 min and was allowed to settle overnight. In order to determine the exchangeable cations, 2.5 g air-dried and sieved soil samples were mixed with 50-mL hexamminecobalt(III)chloride solution (with a soil to 0.016 mol L^{-1} hexamminecobalt(III)chloride solution ratio 1:20, w/v) in 50-mL centrifuge tubes (control samples without soil also prepared and analyzed). The tubes were placed in a shaker for 60 minutes. After shaking, the samples were centrifuged at 4000 rpm min^{-1} for 20 minutes. Lastly, before the analysis with atomic absorption spectroscopy (AAS, AAnalyst 300, Pelkin Elmer), the duplicated samples were filtered through a PTFE filter (0.22 μm).

3.2.2.6. Cation Exchange Capacity (CEC). The cation exchange capacity (CEC) of the soil samples were determined by following the standard Method 9081 of the Environmental Protection Agency (EPA, 1986). 4 g of soil samples were weighed and transferred to 50-mL centrifuge tubes as a first step. Then, the soil samples were mixed with 33 mL sodium acetate (NaOAc) solution in order to result in an exchange between the added sodium cations and the matrix cations. The solution was vortexed for a few minutes and centrifuged at 3500 rpm min^{-1} for 5 minutes until the supernatant part was clear. This step was repeated three more times. In order to wash the soil samples isopropyl alcohol (2-propanol) was used. The solution was vortexed for a few minutes and centrifuged at 3500 rpm min^{-1} for 5 minutes until the supernatant part was clear. Washing was repeated two more times. Washing step was followed by the addition of a 33 mL ammonium acetate (NH_4OAc) solution with an aim of replacement of adsorbed sodium with ammonium. The solution was vortexed and centrifuged as it is mentioned before. The effluents of each NH_4OAc solution were transferred to 100-mL volumetric flask. Finally, the combined washing was analyzed by atomic adsorption spectroscopy (AAS, AAnalyst 300, Pelkin Elmer), the triplicated samples were filtered through a PTFE filter (0.22 μm).

3.2.2.7. Electrical Conductivity (EC). In order to determine the electrical conductivity of the soil samples the standard method of Food and Agriculture Organization of the United Nations (FAO, 2021) was followed (FAO, 2021). As a first step 5 g of soil sample was transferred to a 50-mL centrifuge tube and then the volume was made up to 25 mL by adding DI water with a 1:5, w/v soil to water ratio. Duplicate samples were placed in the shaker horizontally for 60 minutes at 100 rpm. After the shaking, the samples were let stand for 30 minutes. Conductivity meter was placed into the supernatant part without disturbing the sediment and as a final step when a stable value is observed it was recorded.

3.2.3. Pesticide Extraction from the Soil Samples

In order to analyze the pesticide levels in the soil samples QuEChERS (quick, easy, cheap, effective, rugged, and safe) method was performed. Association of Official Agricultural Chemists (AOAC Official Method 2007.01) and British Standard Methods (BS EN 15662:2018) are the two listed standards for the evaluation of target pesticide levels. The first step was to select the most proper method for the extraction among these two. For this reason, a 5 g of commercial plant soil was transferred to 50-mL centrifuge tube and hydrated with 5 mL of MS grade water containing 200 µg L^{-1} surrogate standards (methyl-d3-triphenylphosphonium, N-phenyl-1-naphthylamine, Sodium (N-methyldodecanamido) acetate, ethyl paraben) (Reagent 1) and processed. Table 3.6 shows detailed information about the preparation of commercial plant soil for the extractions. Selection of the method was determined by the comparison of the recovery efficiencies of these two methods.

Table 3.6. Sample identification and ingredients

Sample Name	Sample Tag	Sample Ingredient
AOAC QuEChERS 1	**A1**	5g soil + 5mL Reagent 1 + 10mL Reagent 2
AOAC QuEChERS 2	**A2**	5g soil + 5mL Reagent 1 + 10mL Reagent 2
AOAC QuEChERS 3	**A3**	5g soil + 5mL Reagent 1 + 10mL Reagent 2
British QuEChERS 1	**B1**	5g soil + 5mL Reagent 1 + 10mL Reagent 2
British QuEChERS 2	**B2**	5g soil + 5mL Reagent 1 + 10mL Reagent 2
British QuEChERS 3	**B3**	5g soil + 5mL Reagent 1 + 10mL Reagent 2
AOAC QuEChERS Control	**CtrlA**	5g soil + 5 mL HPLC grade H_2O + 10mL Reagent 2
British QuEChERS Control	**CtrlB**	5g soil + 5 mL HPLC grade H_2O + 10mL Reagent 2
AOAC Reference 1	**R1A**	5 mL HPLC grade H_2O + 5mL Reagent 1 + 10mL Reagent 2
British Reference 1	**R1B**	5 mL HPLC grade H_2O + 5mL Reagent 1 + 10mL Reagent 2
British Reference 2	**R2B**	10 mL HPLC grade H_2O + 10mL Reagent 2
AOAC Reference 2	**R2A**	10 mL HPLC grade H_2O + 10mL Reagent 2

Briefly, while for the AOAC QuEChERS method, 10 mL of acetonitrile containing 1% acetic acid extraction solvent was used, as an extraction solvent acetonitrile with 5% formic acid was used for the British method (Reagent 2). After the addition of the extraction solvents the content was left to agitate on a rotary shaker (100 rpm) at room temperature overnight. On the other hand, for the salting-out step of extraction solvent (acetonitrile phase) for the AOAC method 4 g magnesium sulfate and 1 g sodium acetate and for the British method 4 g anhydrous magnesium sulfate, 1 g sodium chloride, 1 g trisodium citrate dihydrate and 0.5 g disodium hydrogen citrate sesquihydrate were added into the tube and centrifuged at 3500 rpm for 5 min after vigorous shaking. As a final step, a 250 µL supernatant was combined with 250 µL of methanol containing 0.1% formic acid and 5 mM ammonium formate, and 500 µL of water with 0.1% formic acid and 5 mM ammonium formate and the samples were filtered through a 0.22 µm PTFE filter before injection to liquid chromatography-mass spectrometry (LC-MS) for the analysis. Figure 3.4. demonstrates the main differences between the two methods.

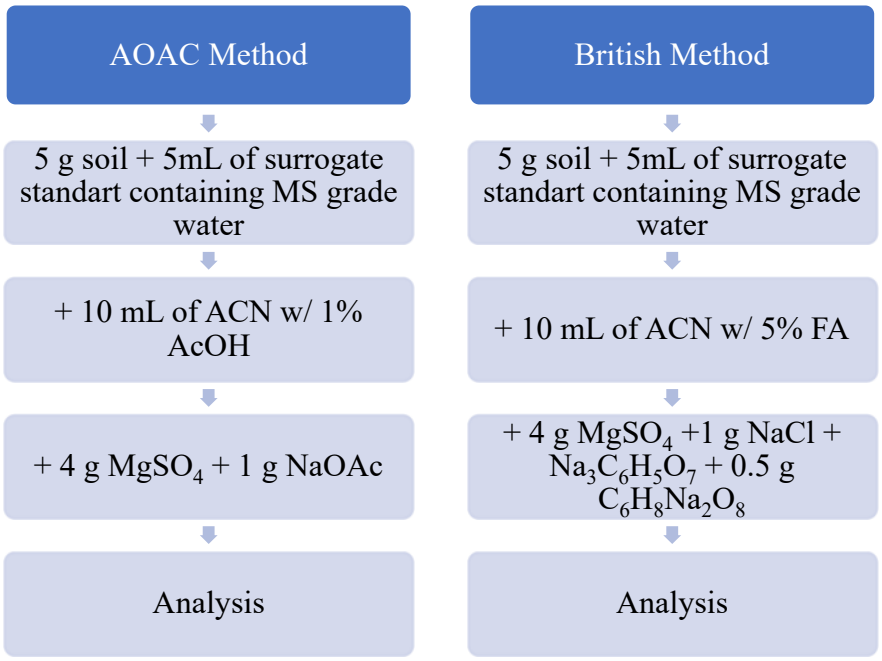


Figure 3.4. Fundamental differences between the AOAC and the British QuEChERS modified methods

3.2.4. LC-MS/MS Analysis of Pesticide Residues in the Soil Samples

For the analysis of the target and untargeted pesticides, AB SCIEX QTrap 4500 linear ion trap tandem mass analyzer system (MS) coupled with Eksigent Ekspert UltraLC 110 ultra-high-performance chromatography (UHPLC) unit (AB SCIEX, Framingham, MA, USA) was used as a part of liquid chromatography with electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS). Multiple reaction monitoring (MRM) was selected as an operation mode of the MS/MS system.

The working principle of the mass spectroscopy is based on the measurement of the mass-to-charge ratio (m/z). For this purpose, a molecule has to be ionized by protonation or deprotonation. Ionized molecule that has a mass of ±1 Da difference from the mass of a unionized molecule is called a parent ion (Q1)(Andreu & Pic, 2004; Rajski et al., 2019; Sack et al., 2015). Figure 3.5. demonstrates the workflow of the determination of the parent ion of the target chemicals to be analyzed.

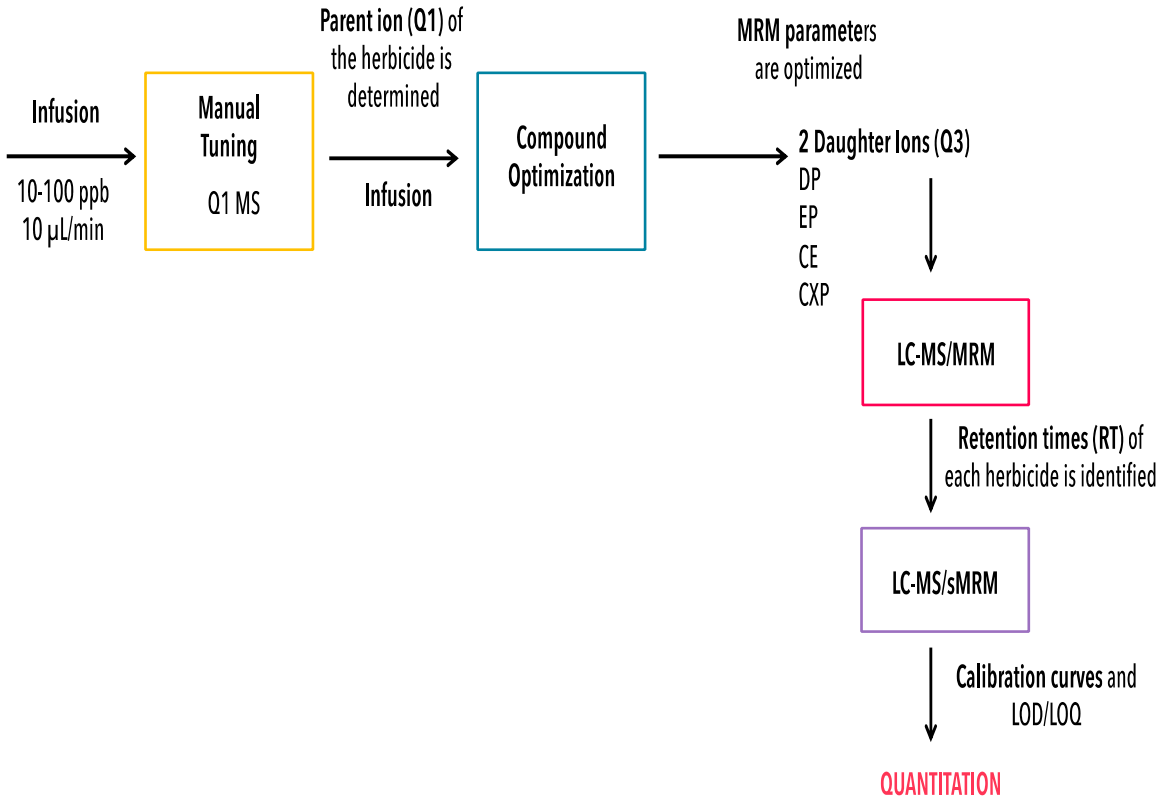


Figure 3.5. Workflow of MRM transitions in LC-MS/MS

3.2.4.1. Analysis of target pesticides. For the determination of the parent ion (Q1) and the surrogate standards, a working solution with a 10-100 µg/L analyte concentration was manually infused at a flow rate of 10 µL/min with an integrated syringe pump into the mass detector (MSD). Operation mode of MSD was "Q1 Mass Scanning" and as the ionization source, electrospray ionization (ESI) was used. The working parameters for MSD were as follows: Curtain gas flow (CUR): 20, Declustering Potential (DP): +70V (for positive ionization) or -50V (for negative ionization), IonSpray Voltage (IS): +5500 (for positive ionization) or -4500 (for negative ionization), Gas1 (GS1): 20, Gas2 (GS2): 0 Temperature (TEM): 0, Colissionally Activated Dissociation Gas Flow (CAD): Low.

After the determination of the parent ions (Q1) of each chemical, 2 daughter ions (Q3s), which are the ions with the highest intensities among the other ions generated after the fragmentation of the parent ion in the collision cell, as well as optimum declustering potential (DP), collusion energy (CE) and collision cell exit potential (CXP) to generate those Q3s were determined by operating MSD in "Compound Optimization" mode. A 10-100 µg/L of analyte was infused into MSD at a flow rate of 7 µL/min and Q3s and optimum conditions for generation of those Q3s were determined by the instrument's default settings for MRM optimization (Figure 3.7). Each Q1 has two Q3 as one is heavy and the other one is light. Heavy Q3 ($Q3_1$) was generated at low collision energies compared to the energy used for the light Q3 ($Q3_2$). Since $Q3_1$ has a greater intensity, it is used for quantitation whereas $Q3_2$ is used for confirmation. Therefore, there is little chance of a chemical that has the same Q1 and the same Q3 pairs, by utilizing the $Q3_2/Q3_1$ ratio and by the help of MRMs, correct identification of the compound of interest in a complex mixture (such as soil) can be achieved.

In order to determine the retention times of the chemicals, chromatographic separation was carried out on ThermoScientific Accucore aQ (100 x 2.1mm) column packed with 2.6 µm particles. MS grade methanol (A) and water (B) having buffered with 0.1% formic acid and 5 mM ammonium formate were used as mobile phases for gradient elution. The column has been operated at a mobile phase constant flow rate of 0.5 mL min^{-1} at a 50 ^{o}C column temperature (Table 3.7).

Table 3.7. Gradient elution parameters for chromatographic separation

Time (min)	**Flow rate (mL min^{-1})**	**A (%)**	**B (%)**
0.00	0.5	10	90
1.50	0.5	10	90
4.00	0.5	60	40
8.00	0.5	70	30
11.00	0.5	100	0
12.00	0.5	100	0

Ionization is operated at ESI probe in positive/negative ionization mode and the operational parameters were as follows: curtain gas, 30; ion spray voltage, 5500 V/ 4500 V; temperature (TEM), 550 ºC; ion source gas 1 (GS1); 50 and ion source gas 2 (GS2), 60. In the APCI mode some parameters were: operated differently as: GS1, 80; GS2, 0 and TEM, 500 ºC. The detection and quantification of the herbicides and surrogate standards were accomplished using the chromatography and mass spectrometry conditions given above with scheduled MRM. For instrumental control, data acquisition, and processing Analyst Software 1.6.2 (AB Sciex) and for the peak control and integration Multiquant 3.0.1 (AB Sciex) were used subsequently.

3.2.4.2. Analysis of non-target pesticides Pesticides, other than the target herbicides, present in the extracts were identified using in-house library containing MRMs of 457 pesticides currently in use in Turkey and enhanced product ion profiling on QTrap 4500 LC-MS system. Firstly, 20 µL soil extracts were introduced into MSD as it was described in the previously mentioned method. The first method scans MRM transitions for 457 pesticides given to the MSD in the sample at 2 ms dwell time (Figure 3.7). Identification of Q3s specific to a certain pesticide in the MRM list indicates the presence of that pesticide in the sample extract. In the second method, linear ion trap and information dependent acquisition (IDA) were used to obtain fragmentation pattern of most intense parent ions eluted during the LC run time. The fragmentation patterns obtained were quarried against the pesticide library and used for the confirmation of pesticides identified in the first method (Figure 3.6). In both methods, MSD settings were same as the method used for the targeted analysis of the herbicides.

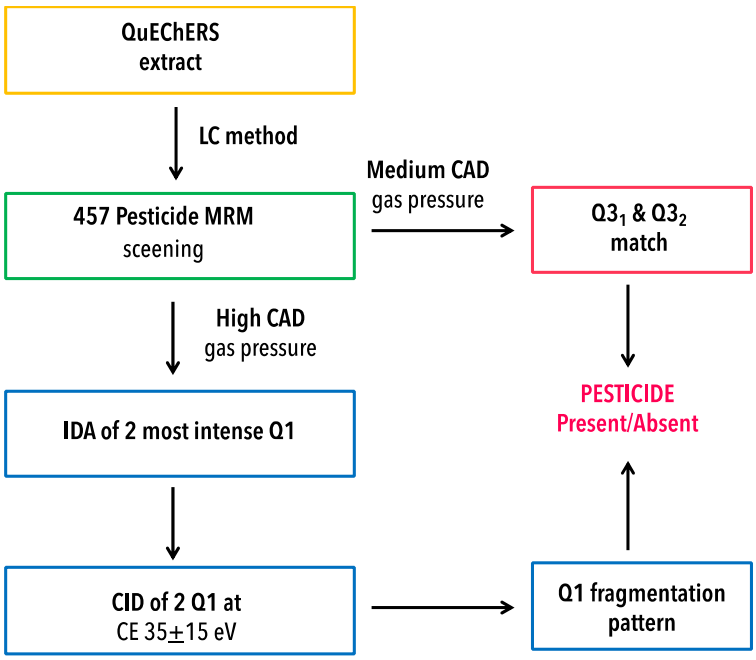


Figure 3.6. Workflow for identification of pesticides in the soil extracts

3.2.5. Batch Experiments

Batch experiments were conducted to determine the chemical retention (adsorption) characteristics of the selected herbicides. Pure form of 2,4-dichlorophenoxyacetic acid (2,4-D) that was purchased from Sigma Aldrich and commercial fenoxaprop-p-ethyl (Fenox) were used in these experiments. Figure 3.7 shows the experimental setup of sorption tests for the target pesticides. It has been worked with duplicate samples for each selected herbicide.

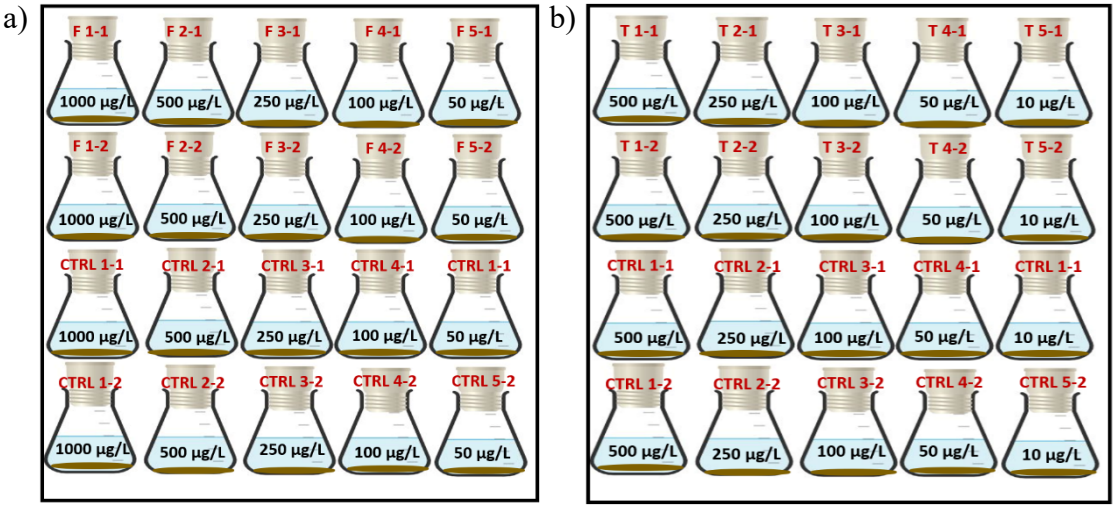


Figure 3.7. Experimental setup for a) Fenox and b) 2,4-D

3.2.5.1. Sorption of 2,4-dichlorophenoxyacetic acid. In order to prepare a 50.000 mg L^{-1} stock solution 0.5 g of technical 2,4-D was dissolved in 10 mL MeOH (1:20, w/v). In order to obtain a 500 mg L^{-1} working solution, the stock solution was diluted two times in 10 mL MeOH (1:10, v/v). Working pesticide solutions of five different concentrations (10, 50, 100, 250, and 500 µg L^{-1}) were prepared by adding 0.02, 0.10, 0.20, 0.50, and 1.00 mL of 500 mg L^{-1} working solution respectively to 1-L volumetric flasks. Before the addition of working pesticide solutions of five different concentrations, 1.5 g of soil was added to 250-mL Erlenmeyer flasks. After the addition of the soil samples, 150 mL of each working pesticide solution was transferred to the 250-mL Erlenmeyer flasks that contained soil samples. Erlenmeyer flasks were closed with caps and placed on the orbital shaker at 100 rpm. Samples were taken as a volume of 2 mL at the 0., 2, 4, 8, and 24 hours. Only 0. hour samples were taken before placing the flasks on the orbital shaker. After getting the samples to the 50-mL centrifuge tubes, all the samples were subjected to centrifugation at 3500 rpm at 5 min. At the end of the centrifugation, 2 mL supernatants were transferred to new 50-mL centrifuge tubes then organic solvents ACN, MeOH and IS mixture were added as 2 mL of each. Then the mixture was filtered through a 0.22 µm syringe and transferred to 15-mL centrifuge tubes. As a final step, 1.5 mL of the filtered samples were transferred to amber GC-vials and were given to LC/MS-MS.

3.2.5.2. Sorption of fenoxaprop-p-ethyl. In order to prepare a 690 mg L^{-1} working pesticide solution, a 1mL of commercial fenox with a concentration of 69 g L^{-1} was dissolved in 10 mL of MeOH (1:10, v/v) respectively three times. Working pesticide solutions of five different concentrations (50, 100, 250, 500, and 1000 µg L^{-1}) were prepared by adding 0.07, 0.14, 0.36, 0.72, and 1.45 mL of 690 mg L^{-1} working solution respectively to 1-L volumetric flasks. Before the addition of working pesticide solutions of five different concentrations, 1.5 g of soil was added to 250-mL Erlenmeyer flasks. After the addition of the soil samples, 150 mL of each working pesticide solution was transferred to the 250-mL Erlenmeyer flasks that contained soil samples. Erlenmeyer flasks were closed with caps and placed on the orbital shaker at 100 rpm. Samples were taken as a volume of 2 mL at the 0, 2, 4, 8, and 24 hours. Only 0-hour samples were taken before placing the flasks on the orbital shaker. After getting the samples to the 50-mL centrifuge tubes, all the samples were subjected to centrifugation at 3500 rpm at 5 min. At the end of the centrifugation, 2 mL supernatants were transferred to new 50-mL centrifuge tubes then organic solvents ACN, MeOH and IS mixture were added as 2 mL of each. Then the mixture was filtered through a 0.22 µm syringe and transferred to 15-mL centrifuge tubes. As a final step, 1.5 mL of the filtered samples were transferred to amber GC-vials and were given to LC/MS-MS.

3.2.6. Column Experiments

For the column transport experiments, a glass column with dimensions 1.4 cm inner diameter and 20 cm length was used as a packed column. The column was filled with soil/sand (3:7, w/w) mixture and it was connected to a peristaltic pump with variable speed control to maintain the desired flow rates (Figure 3.8). Teflon tubings were used for the connections. This soil to sand ratio was selected due to the low permeability of the soil (Limousin et al., 2007). The column was connected to a fraction collector in order to collect the samples at desired time intervals. Water flow was set to be vertically upwards and effluent samples were collected from the top. Two different experimental set-ups were conducted due to different sorption patterns of the selected herbicides. Firstly, a non-reactive tracer test with 0.01 M NaCl solution was applied at two different flow rates as 0.75 mL min^{-1} and 1.0 mL min^{-1} for the 2,4-D column, and the EC of the collected effluent samples were measured with conductivity meter in order to determine the dispersion coefficient. For the Fenox column, the tracer test was applied only at 1.0 mL min^{-1} flow rate. For the preparation of 0.01 M NaCl solution, it needed 0.01 moles of NaCl in a total volume of 1 liter. So, 0.584 g of oven-dried NaCl was dissolved in 1-L volumetric flask and the volume was made up 1-L by adding DI water.

In order to estimate the dispersion coefficient and dispersivity, the data obtained from the tracer test was fitted to the 1D advection dispersion equation given by (Equation 3.4):

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial Z^2} - V\frac{\partial C}{\partial Z} \tag{3.4}$$

Where,

V velocity
C tracer concentration function of x (distance and t (time))
D hydrodynamic dispersion coefficient
∂ dispersivity

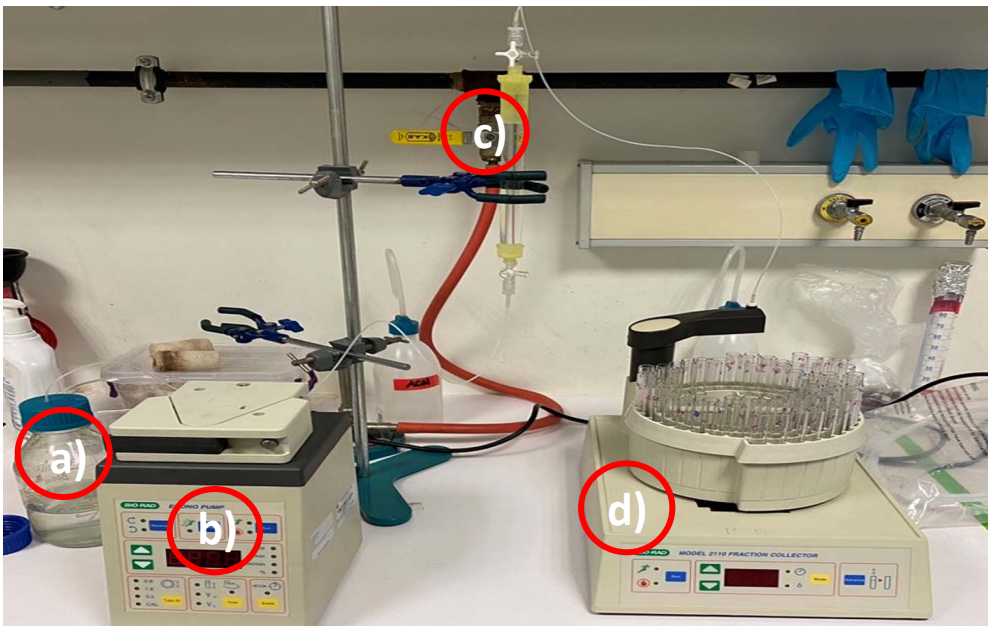


Figure 3.8. Experimental setup for the column transport experiments: a) feed reservoir b) peristaltic pump c) glass column d) fraction collector

For the column transport experiment of 2,4-D, firstly by dissolving 0.5 g of technical 2,4-D in 10 mL MeOH (1:20, w/v) a 50.000 mg L^{-1} stock solution of 2,4-D was prepared. In order to obtain a 500 mg L^{-1} working solution, the stock solution was diluted two times in 10 mL MeOH (1:10, v/v) as previously prepared in the batch experiments. The column was loaded only with the 500 µg L^{-1} 2,4-D solution. The soil length in the column was 12.5 cm and the mass of the soil mixture was 30 g. The flow rate was set to be 0.75 mL min^{-1} and the composite samples were collected as 3 min. fractions during 2 hours.

For the column transport experiment of Fenox, in order to prepare 690 mg L^{-1} working pesticide solution, a 1mL of commercial Fenox with a concentration of 69.000 mg L^{-1} was dissolved in 10 mL of MeOH (1:10, v/v) and then 6900 mg L^{-1} solution was dissolved again in 10 mL of MeOH (1:10, v/v). The column was loaded only with the 500 µg L^{-1} Fenox solution. The soil length in the column was 10 cm and the mass of the soil mixture was 20 g. The flow rate was set to be 1.0 mL min^{-1} and the samples were collected twenty-one times. The test duration was one week.

4. RESULTS AND DISCUSSION

4.1. Soil Characterization

A total of 17 agricultural soil samples were collected from 4 different fields of the agricultural farm: (i) wheat, (ii) rotation of wheat/corn, (iii) barley, (iv) apple and from an uncultivated land (background). For the batch and column experiments, a mixture from samples #12-12-14 were used. Prior to the evaluation of the fate and transport behavior of the pesticides, some physical and chemical properties such as soil texture, cation exchange capacity (CEC), pH, electrical conductivity (EC), soil moisture were analyzed and the results are presented in this chapter.

4.1.1. Soil Moisture

Since air-dried soil samples were used in most of the experiments and it was important to know the moisture content of the soil samples for further evaluations, water content of the collected samples was determined at the very beginning of the study. The soil moisture loss was recorded continuously at two-day intervals and the whole air-drying process took 18 days until a stabilization occurred in weight loss for all the agricultural soil samples (Figure 4.1.). An average starting weight, amount loss and % reduction was 105.15 grams, 16.75 grams and 15.93 % for the samples respectively (n = 17). Weight loss stabilization was observed at between 85 and 90 grams for all the samples (n = 17) (Figure 4.1.). After the air-drying process, the moisture content of the air-dried soil samples was controlled by igniting the soil samples in a muffle furnace at a temperature of 105 °C. The moisture content of the samples was found to be between 1.6 and 5.3 % of the total weight. Since the water content of the soil samples was lower than 6 %, it was determined that the QuEChERS method could be applied.

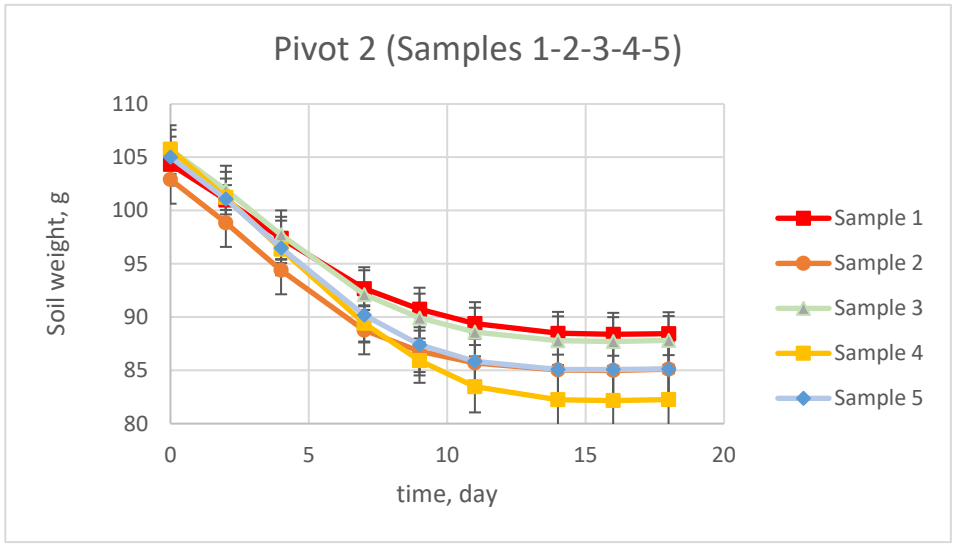
Table 4.1. Soil Drying (n=17)

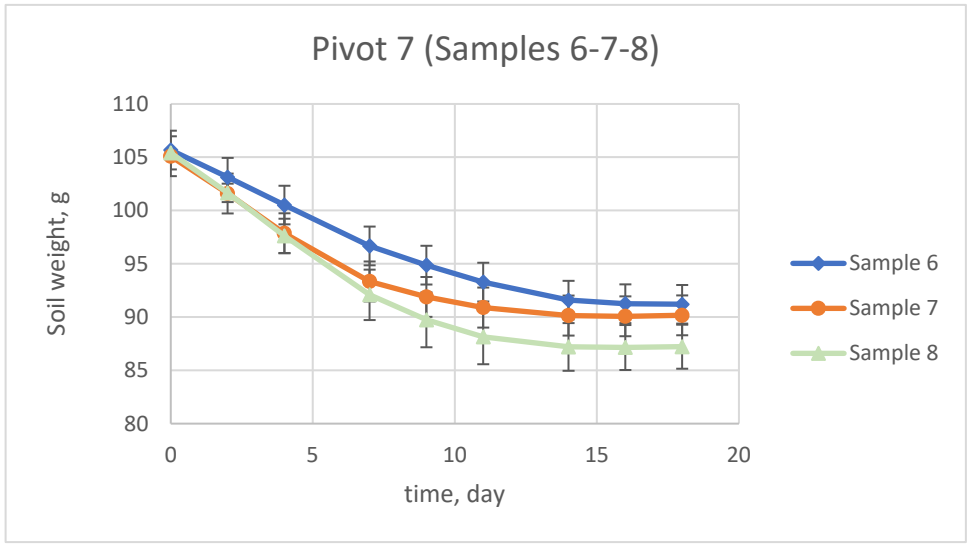
Sample#	Sample Weight (g)	Amount Loss (g)	%Reduction	Time (day)
1	104.34	15.90	15.24	18
2	102.90	17.78	17.28	18
3	105.71	17.90	16.94	18
4	105.75	23.51	22.23	18
5	105.01	19.88	18.93	18
6	105.67	14.46	13.69	18
7	105.09	14.93	14.21	18
8	105.40	18.17	17.24	18
9	105.16	15.39	14.63	18
10	105.53	14.34	13.59	18
11	104.59	16.97	16.23	18
12	105.76	11.71	11.07	18
13	105.67	15.18	14.36	18
14	104.45	15.28	14.63	18
15	105.36	15.19	14.42	18
16	105.93	20.09	18.96	18
17	105.24	18.08	17.18	18
Mean	105.15	16.75	15.93	-

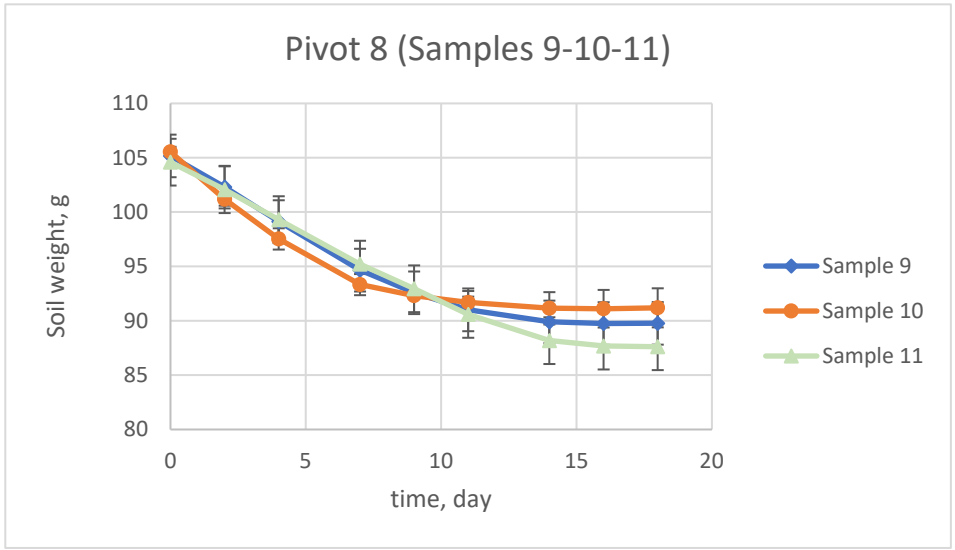
Also, in order to determine the moisture content of the soil samples, a weight (5 g) of the duplicate samples were evaporated to a constant weight condition for 24 hours, in an oven maintained at a temperature of 105 °C. The moisture content of the raw samples was between 11.1 and 24.0% of the total weight with a median equal to 17.0 % (n = 17) (Table 4.2.).

Table 4.2. Moisture content of the soil samples after oven drying at 105 °C (mean±standard dev., n=2)

Sample#	Moisture (%)
1	17.30±0.47
2	19.53±0.12
3	16.90±2.38
4	24.02±1.19
5	21.00±0.33
6	15.43±0.00
7	15.95±0.40
8	18.36±0.18
9	16.99±0.06
10	15.50±0.37
11	20.56±0.91
12	11.11±0.46
13	16.51±0.15
14	16.17±0.26
15	16.66±0.15
16	20.94±0.03
17	19.29±0.00







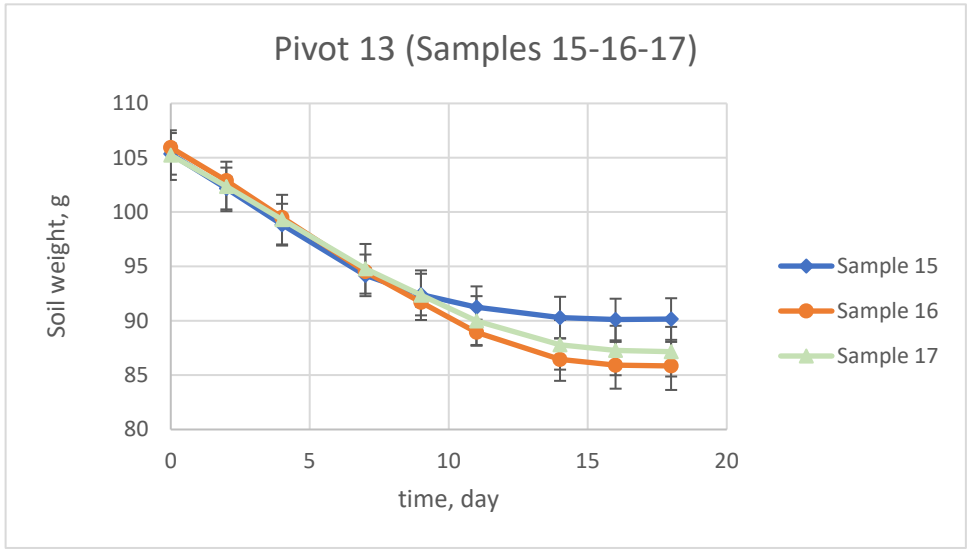


Figure 4.1. Weight loss of the collected samples

Since the uncultivated land was free of recent pesticide application, it was decided to use the mixture of the soil samples (samples 12,13,14) (*n*=3) collected from this area in the batch and column studies. This would reduce the presence of bacground pesticide contamination which would complicate the interpretation of the experiments. The selected soil samples also had similar soil moisture characteristics with the other agricultural soil samples (Figure 4.2). The water content of the soil mixture that was used in the batch and column experiments was 13.7±0.6 % and the organic content was 3.0±0.06.

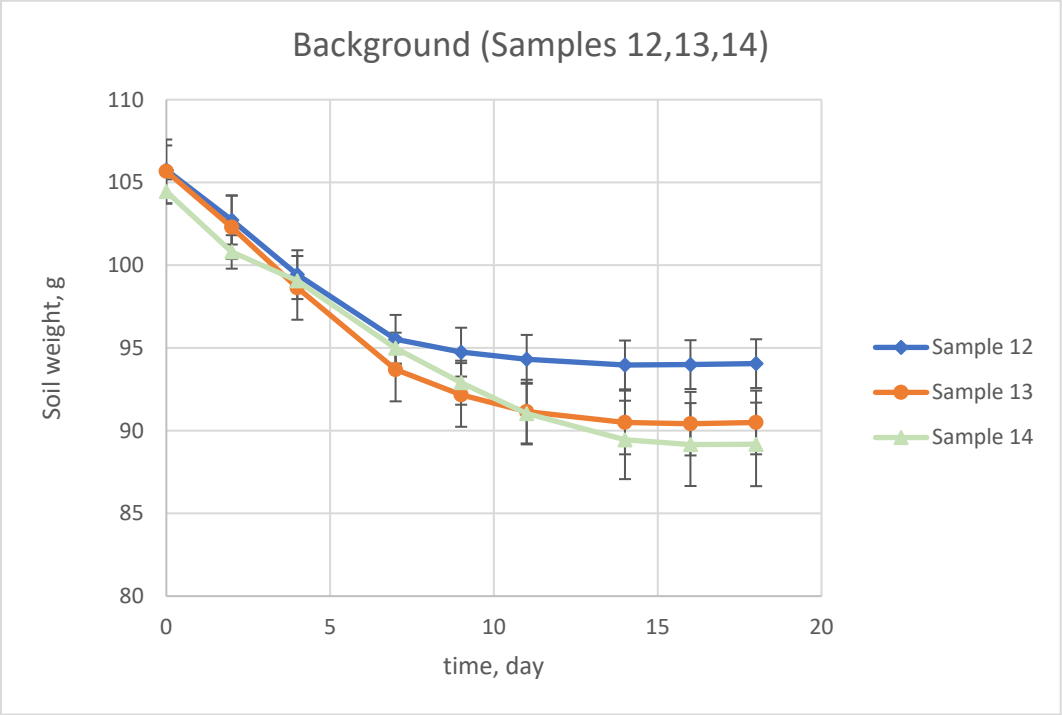


Figure 4.2. Moisture loss of the samples 12,13, and 14 due to evaporation

4.1.2. Total and Volatile Solids

Total solids were calculated from the moisture content using the following relation (Equation 4.1):

$$\% \text{ Total solids} = 100 - \% \text{ Moisture} \quad (4.1)$$

The total solid content of the samples was between 76.0 and 88.9% with a median equal to 83.0%.

Table 4.3. Solid content of the soil samples (mean±standard dev., n=2)

Sample#	Solid content (%)
1	82.69±0.47
2	80.47±0.12
3	83.09±2.38
4	75.97±1.19
5	78.99±0.33
6	84.56±0.00
7	84.04±0.40
8	81.64±0.18
9	83.01±0.06
10	84.50±0.37
11	79.44±0.91
12	88.89±0.46
13	83.48±0.15
14	83.83±0.26
15	83.34±0.15
16	79.05±0.03
17	80.70±0.00

4.1.3. pH, EC, Sive Analysis, and Moisture and Organic Content of the Soil Mixture

The $pH_{(KCl)}$ of the soil mixture (#12-13-14) was measured as 8.07±0.01 at 20.0±1ºC, which could be classified as moderately alkaline soil. In addition, the pH values of all the 17 soil samples were in the range of 7.46-8.18. Solubility of the nutrients is highly dependent on soil pH and at an alkaline pH despite the calcium and magnesium content being more dominant, the abundance of essential metals, also phosphorus and boron, can be insufficient (Muckel & Mausbach, 2015). Furthermore, the moisture content of the soil mixture was found to be 13.7 % while the organic content was found to be 3.0 %. It was reported in the literature that the pH and the organic content of the silty clay loam and silty clay soils in the Konya Plain (38º 05′ north latitudes and 32º 36′ east longitudes) as 7.75-7.79 and 1.84-1.36% respectively (D. Yavuz et al., 2020). These values are consistent with the data observed in the current study. The EC of the soil mixture (#12,13,14) was determined as 142.6±2.9 µs cm^{-1}. Ozaytekin et al. (2012) also measured similar soil EC values with the soils that have a similar organic content and a texture in Çumra region (Ozaytekin et al., 2012). It is stated that if the EC value of a soil sample is between 0-2 dS m^{-1} (0-2000 µs cm-1), it can be classified as non-saline (Gorji et al., 2020).

Figure 4.3 presents the particle size distribution curve of the soil mixture. It was calculated that 86.3% of the soil content was sand, 13.7% fine particles (silt and clay), and 0.00% gravel. According to the United States Department of Agriculture (USDA) textural triangle, the texture of the soil mixture was clarified as loamy sand (USDA, 1987). A summary of the soil characteristics of the soil mixture (#12-13-14) can be seen from Table 4.4.

Table 4.4. Characterization of the soil samples used for the batch and column experiments (mean±standard dev., n=2)

Sample	CEC (mEq 100 g^{-1})	EC (µs cm^{-1})	pH (KCl)	Soil texture	Moisture content (%)	Organic content (%)
#12,13,14	29.08	142.6±2.9	8.07±0.01	Loamy sand	13.7±0.57	3.0±0.06

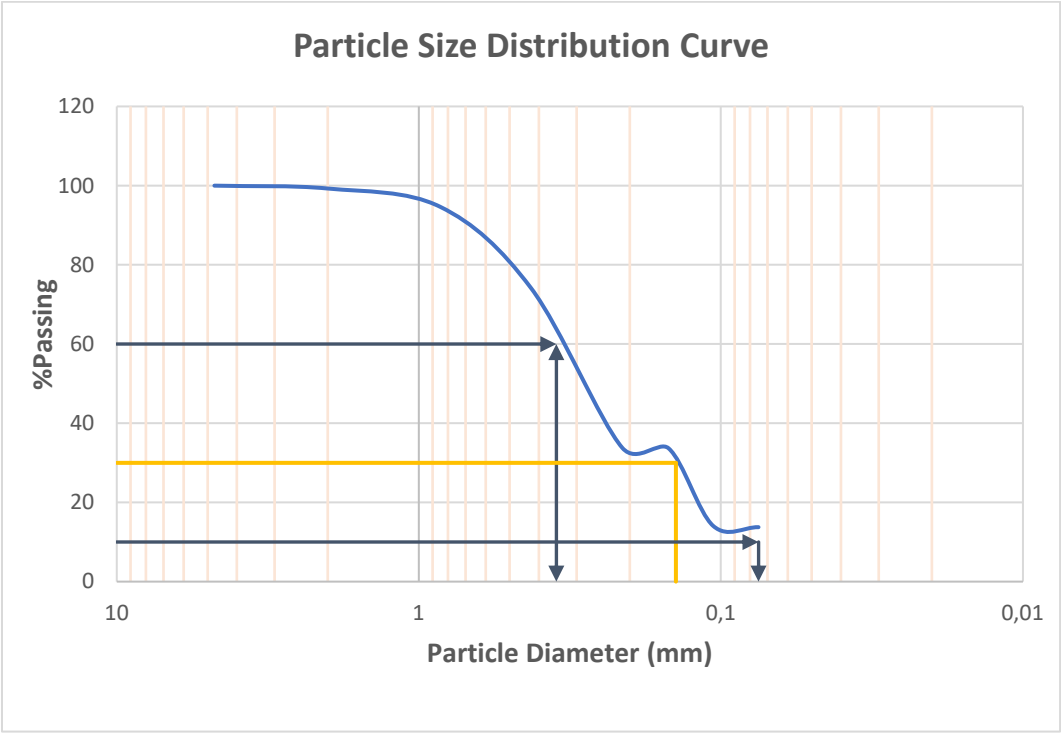


Figure 4.3. Particle size distribution of the soil mixture that is used for the batch and column studies

4.1.4. Cation Exchange Capacity (CEC) and Exchangeable Cations

The CEC is defined as milliequivalent grams of exchangeable cations in 100 g of soil (Rhoades, 2011). The CEC of the soil samples was analyzed by using atomic absorption spectroscopy (AAS).

Table 4.5 shows the measured concentrations of the exchangeable cations such as Na^+, K^+, Mg^{2+} and Ca^{2+}.

Table 4.5. Exchangeable cation concentrations (mean±standard dev., n=3)

Na^+ (mg L^{-1})	K^+ (mg L^{-1})	Mg^{2+} (mg L^{-1})	Ca^{2+} (mg L^{-1})
1883.0±0.05	48.3±0.01	259.2±0.07	3715.2±1.8

In order to determine CEC, it is necessary to convert measured concentrations to mEq 100 g^{-1} dividing by the atomic weight and valance number of each cation (Table 4.6).

Table 4.6. Conversion factors for the most common exchangeable cations (Reganold & Harsh, 1985).

	Na^+	K^+	Mg^{2+}	Ca^{2+}
Valance number	1	1	2	2
Atomic weight	22.9	39.0	24.0	40.0
Gram equivalent weight	22.9	39.0	12.0	20.0
mEq 100 g^{-1} (soil)	**229**	**390**	**120**	**200**

The conversion of measured concentrations to mEq 100 g^{-1} is then calculated by the formula (Equation 4.2):

$$\text{CEC (mEq 100 g}^{-1}\text{)} = \text{mg L}^{-1}\text{/ mEq 100 g}^{-1}\text{ (soil)} \quad (4.2)$$

Table 4.7. CEC value of the soil sample

Na^+ (mEq 100 g^{-1})	K^+ (mEq 100 g^{-1})	Mg^{2+} (mEq 100 g^{-1})	Ca^{2+} (mEq 100 g^{-1})	Total (mEq 100 g^{-1})
8.22	0.12	2.16	18.58	**29.08**

The calculated CEC value can be seen from the Table 4.7.

4.2. Evaluation of the Extraction Method of Pesticides from the Soil Samples

For the extraction of selected herbicides, i.e., 2,4-dichlorophenoxyacetic acid (2,4-D) and fenoxaprop-p-ethyl (Fenox), “quick, easy, cheap, effective, rugged, and safe” QuEChERS method

was applied. As a result of the spiking of the commercial plant soil with 1µg of each surrogate standard and herbicide and extraction with both AOAC and BS methods following the procedure described in the Materials and Methods chapter. Obtained extracts from the two methods were analyzed using the LC-MS settings given in Table 4.8 with the sMRM parameters optimized for each chemical substance.

Table 4.8. sMRM parameters for surrogate standards and target herbicides

Compound	**Transition**	**R_t**	**DP**	**EP**	**CE**	**CXP**
Pos 1	280.1→107.9 280.1→261.8	4.85 4.85	96 96	10 10	47 43	10 10
Pos 2	220.0→91.8 220.0→115.0	9.27 9.27	86 86	10 10	29 67	8 6
Fenoxaprop-p-ethyl	361.9→287.8 361.9→76.9	9.78 9.78	116 116	10 10	25 83	6 14
Neg 1	270.1→87.8 270.1→225.5	9.73 9.73	-90 -90	-10 -10	-22 -22	-11 -19
Neg 2	165.0→92.0 165.0→135.7	5.34 5.34	-20 -20	-10 -10	-30 -19	-9 -11
2,4-D	218.9→160.5 218.9→124.5	5.78 5.78	-55 -55	-10 -10	-18 -36	-11 -9

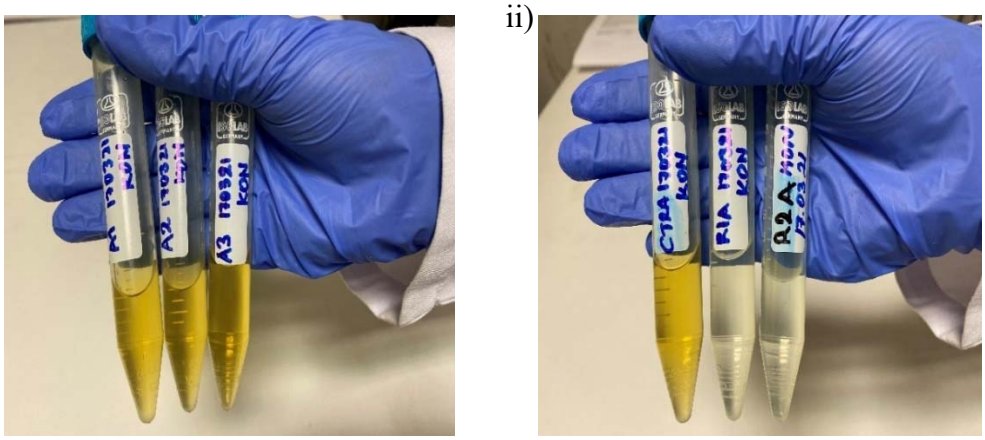
*Pos 1: Methyl-d3-triphenylphosphonium, Pos 2: N-phenyl-1-naphthylamine, Neg 1: Sodium (N-methyldodecanamido) acetate, Neg 2: Ethyl paraben

The mean recovery of surrogate standards and target herbicides from the soil by AOAC and BS methods were 45.4±14.1 and 51.6±28.2% (n=21), respectively (Table 4.9). No significant difference of recovery efficiency was detected between the two methods used for the extraction. Figure 4.4 shows the collected extracts of the two methods. Since the AOAC method is mostly used for the detection of pesticide residues in European soils and attenuated amount of environmental pollution due to lower levels of raw materials were added, the AOAC method was selected to be used for the screening of the target and non-target pesticides for the field soil samples of this study (Lawal et al., 2018; Bragança et al., 2019; Acosta-Dacal et al., 2021).

Table 4.9. Comparison of AOAC and BS methods for the recovery of surrogate standards and herbicides from soil

Compound	AOAC Recovery (%)	BS Recovery (%)
Pos 1	39.5±1.1	53.1±0.3
Pos 2	30.6±1.4	8.3±0.5
Fenoxaprop-p-ethyl	43.6±1.2	46.0±0.4
Neg 1	48.9±0.6	59.3±0.4
Neg 2	43.6±1.9	34.7±0.4
2,4-D	37.2±0.6	58.9±3.9

i) ii)



iii) iv)

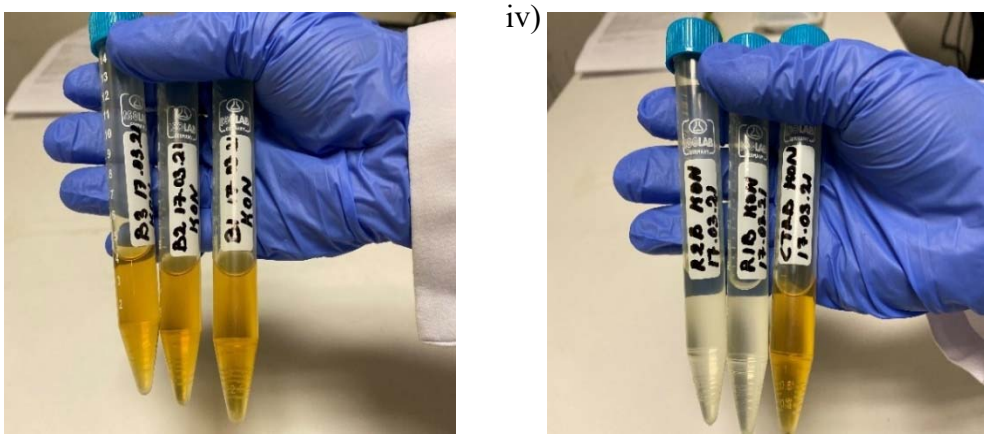


Figure 4.4. i) A1, A2, A3 extracts, ii) CtrlA, R1A, R2A extracts, iii) B1, B2, B3 extracts, vi) CtrlB, R1B, R2B extracts

According to the recovery results, it is observed that the target herbicides can be absorbed by the soil but their sorption behavior can be accurately determined by using the selected surrogate standards. Surrogate standards Pos1 and Neg1 were selected for the calculation of the concentrations of the residues of both negatively and positively ionized target herbicides in soil samples, since the target herbicides in AOAC method and the surrogate standards have similar recovery efficiencies.

4.3. LC-MS/sMRM Method Performance for the Measurement of the Target Herbicides

After the determination of the extraction method and the identification of surrogate standards that would be used in the analysis, calibration curves were constructed and the method's limit of detection (LOD) for each herbicide was calculated. The calibration curve of each herbicide was constructed using concentration and MSD peak area of the herbicide normalized to the selected surrogate standard's concentration and peak area. All the calibration curves were linear within the range of 0.025 to 25 μg L^{-1} or 0.2 to 200 ng g^{-1}-soil with an R^2 greater than 0.998 (Figure 4.5). The method's limit of detection for fenoxaprop-ethyl, and 2,4-D were 0.31, and 0.29 ng g^{-1}-soil, respectively.

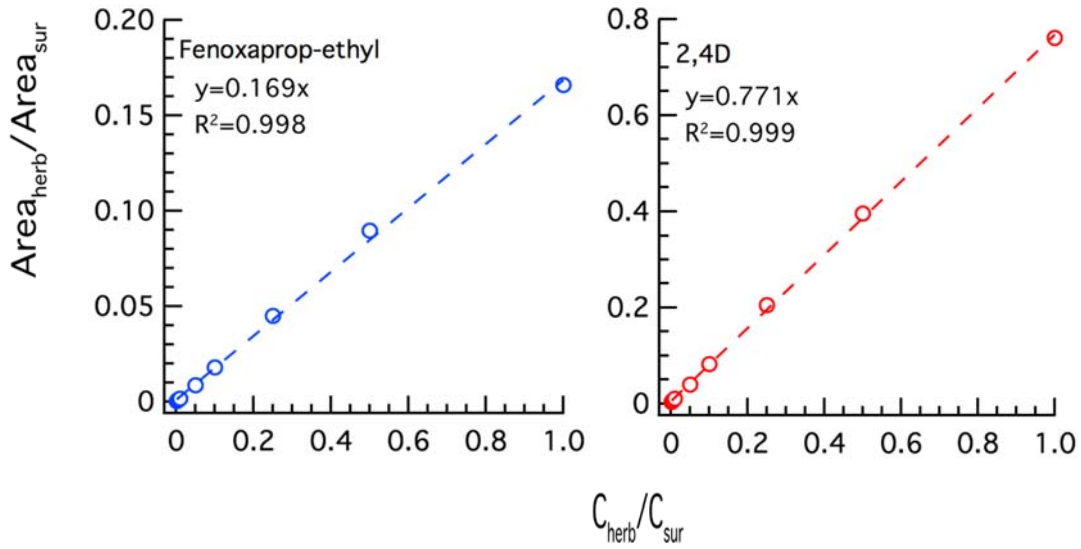


Figure 4.5. Calibration curves of fenoxaprop-ethyl, and 2,4-D

Moreover, non-targeted pesticide analysis workflow was confirmed on a pesticide mixture solution obtained from a National Food Laboratory. Pesticides that existed in the mixture were meticulously detected with the present method. (Figure 4.6). For example, out of 33 negatively ionizable pesticides screened, 14 of them were present in the pesticide mixture obtained from the National Food Laboratory.

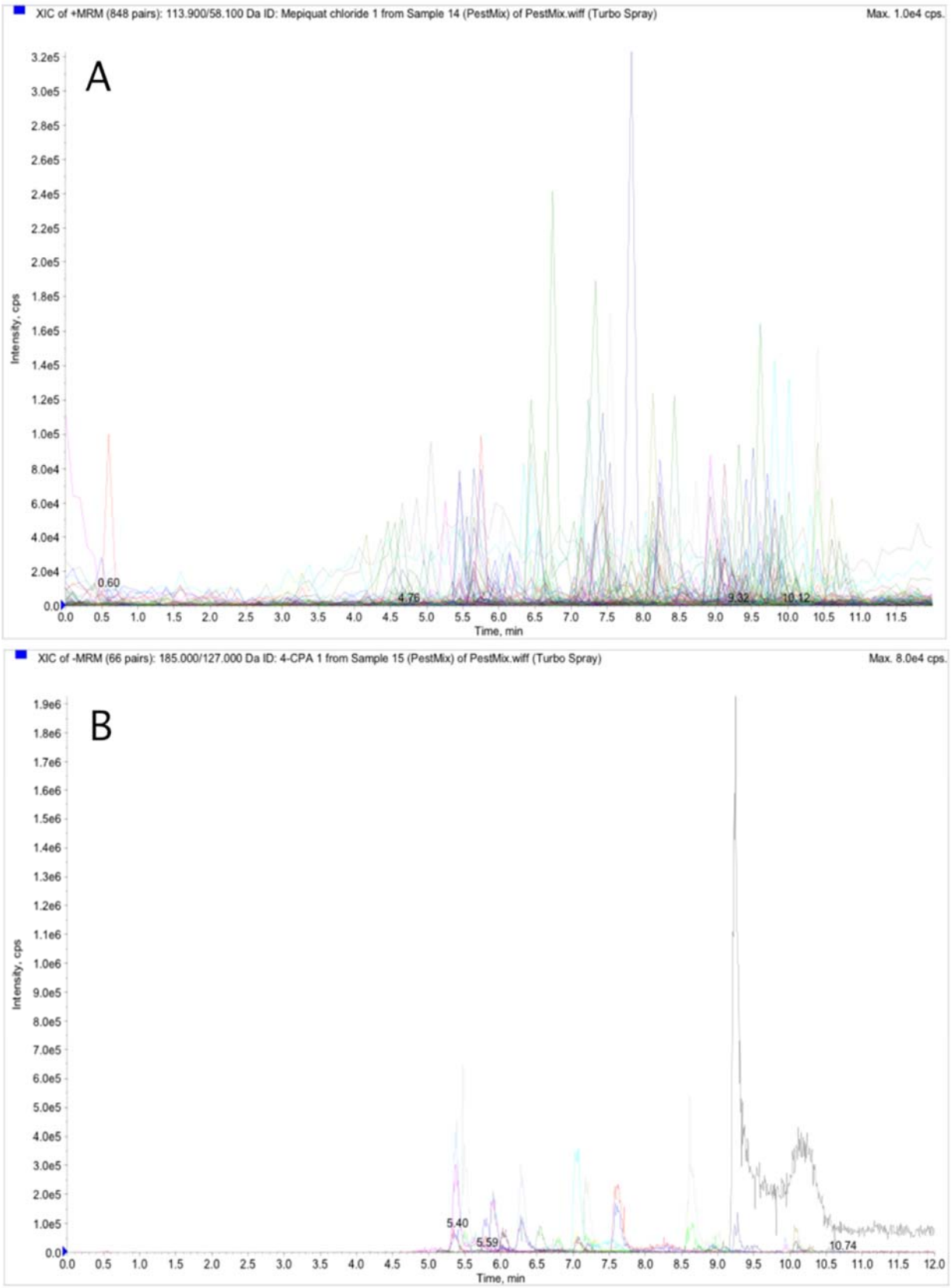


Figure 4.6. Extracted ion chromatogram (XIC) of in-house MRM screening of 457 pesticides in (A) positive and (B) negative ESI ionization modes

4.4. Batch Sorption Experiments

4.4.1. Calibration Curves

In order to determine the sorption characteristics of the selected herbicides, calibration curves were prepared as mentioned above. The calibration curve of each herbicide was constructed using concentration and MSD peak area of the herbicide normalized to the selected surrogate standard's concentration and peak area. All the calibration curves were prepared at a range of 0.1-100 µg L^{-1}. For the calculations, the IS which had the greatest peak area was selected. It was Neg2-2 for the 2,4-D and Pos2-1 for the Fenox. All the calibration curves were linear and the linear regression coefficients (R^2) were greater than 0.990 (Figure 4.7). The division factors selected for 2,4-D and Fenox are 125.01 and 24.644, respectively.

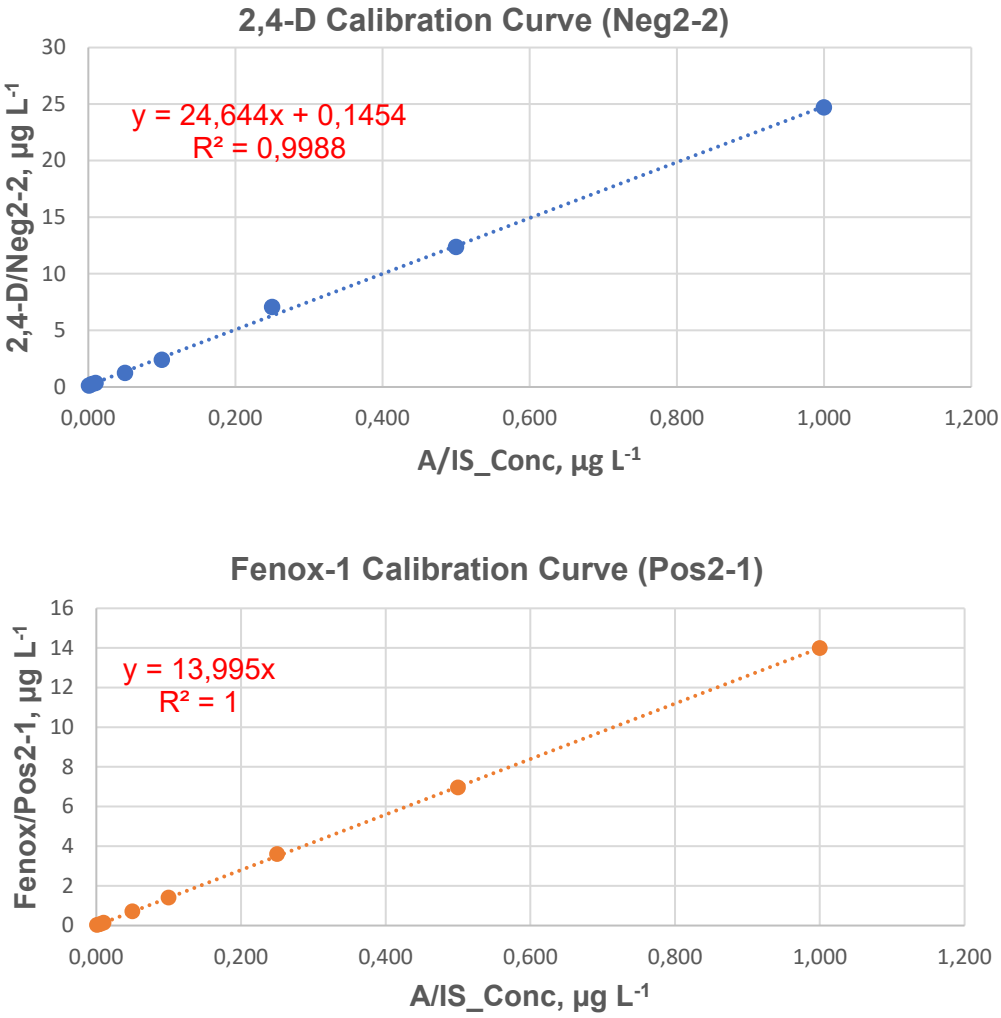


Figure 4.7. Calibration curves of 2,4-D and Fenox

4.4.2. Sorption Kinetics

In order to establish the sorption behavior of the selected herbicides, sorption experiments were conducted. Over time, it is expected to observe a decrease in the initial pesticide concentrations in the aqueous phase due to sorption process. Figure 4.8 shows that the concentration for each initial concentrations remains constant over the duration of the tests, indicating that there was very limited sorption for all the concentrations of 2,4-D. On the other hand, Figure 4.9 shows a clear reduction for Fenox concentration in the aqueous phase for all the prepared concentrations.

In addition to % recovery, prepared and measured concentrations of the selected pesticides are presented in Table 4.10. The recovery of the Fenox measurements was somewhat poor. However, it was observed that very low concentrations such as 2.5 µg L^{-1} could be measured with the current analytical method. The low recovery may be due to the accuracy and pureness of the commercial herbicide solutions used in the experiments. Apart from Fenox, recoveries for each working solution of 2,4-D were between the acceptable recovery limits (70-120%).

Table 4.10. Measured concentrations of the control samples of 2,4-D and Fenox

Pesticide	Aimed conc. (µg L^{-1})	Measured conc. (µg L^{-1})	Recovery (%)
2,4-D	500	517.3	103.5
	250	224.1	89.6
	100	87.8	87.8
	50	37.9	75.8
	10	9.5	94.8
Fenox	1000	45.13	4.51
	500	24.91	4.98
	250	13.33	5.33
	100	4.64	4.64
	50	2.42	4.84

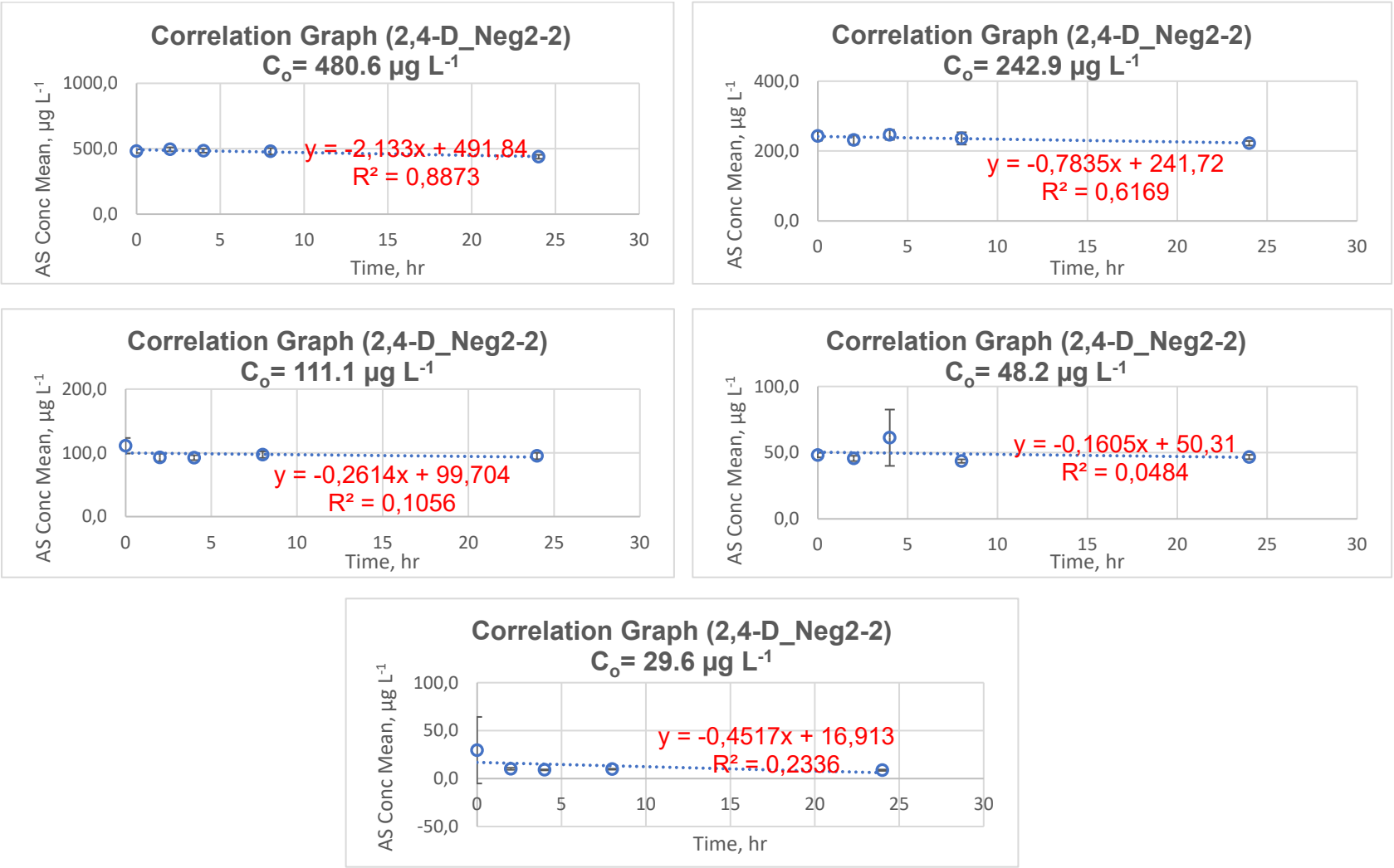


Figure 4.8. 2,4-D aqueous phase concentration as a function of time from the batch tests for different initial concentrations

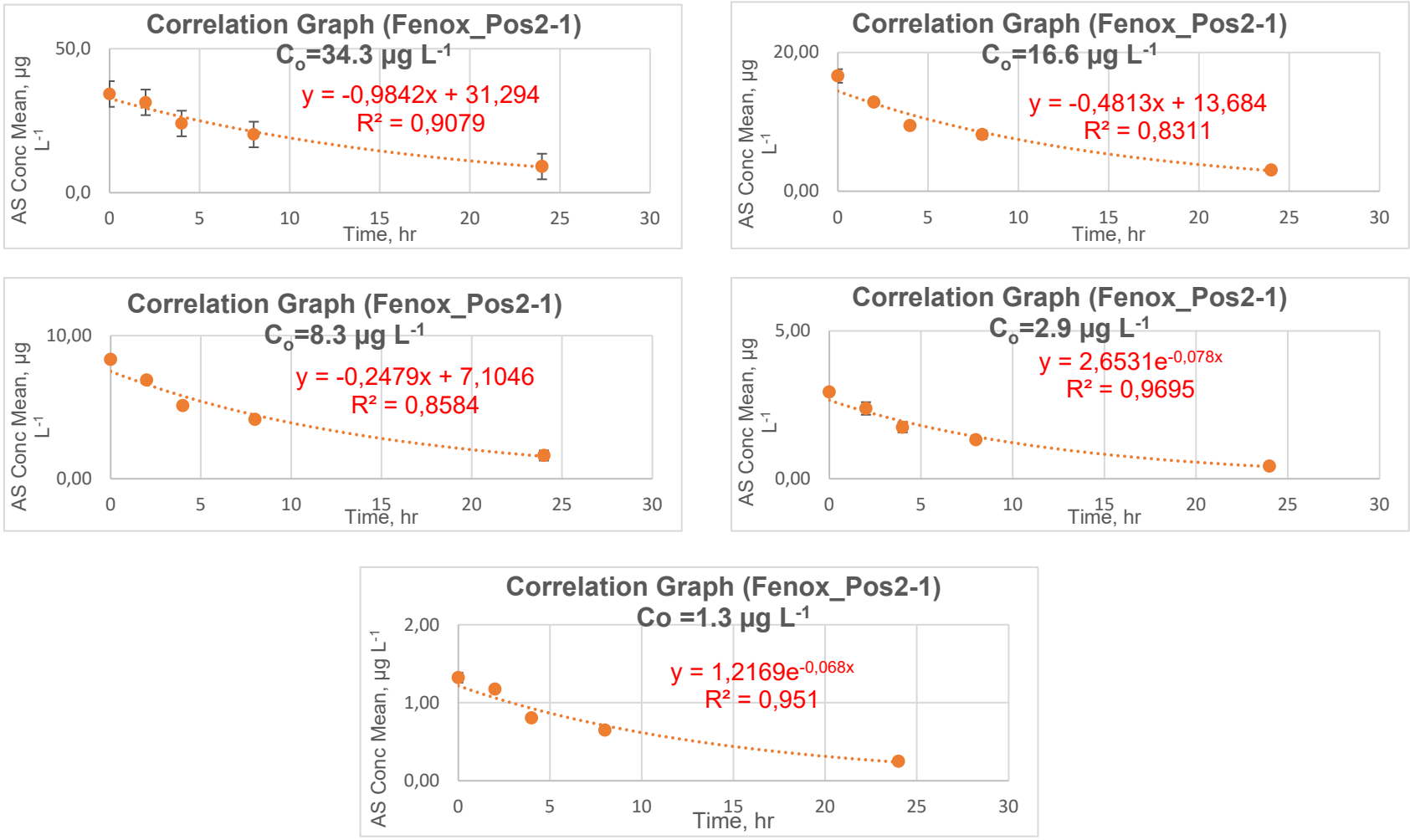


Figure 4.9. Fenox aqueous phase concentration as a function of time from the batch tests for different initial concentrations

The sorbed concentration of the selected herbicides are also presented in Tables 4.11, 4.12, 4.13, and 4.14. Table 4.11, and 4.12 give the sorbed concentrations of 2,4-D at the hours 8 and 24, while Table 4.13, and 4.14 shows the sorbed concentrations of Fenox at the same time. A consistent increase in the sorbed concentrations for Fenox was observed for the hours 8 and 24. This indicates that steady state conditions were not reached after 8 hours. On the other hand, the data obtained for 2,4-D did not indicate a particular trend suggesting very low distribution constant, K_d, of 2,4-D.

Table 4.11. 2,4-D concentration from the batch experiments after 8h

Pesticide	Time (hr)	Mass of soil (g)	Batch test volume (L)	Initial conc. ($\mu g\ L^{-1}$)	Sorbed conc. ($mg\ g^{-1}$)
2,4-D	8	1.5	0.15	480.6	0.0037
2,4-D	8	1.5	0.15	242.9	-0.0012
2,4-D	8	1.5	0.15	111.1	-0.0009
2,4-D	8	1.5	0.15	48.2	-0.0006
2,4-D	8	1.5	0.15	29.6	-0.00003

Table 4.12. 2,4-D concentration from the batch experiments after 24h

Pesticide	Time (hr)	Mass of soil (g)	Batch test volume (L)	Initial conc. ($\mu g\ L^{-1}$)	Sorbed conc. ($mg\ g^{-1}$)
2,4-D	24	1.5	0.15	480.6	0.0079
2,4-D	24	1.5	0.15	242.9	0.002
2,4-D	24	1.5	0.15	111.1	-0.0007
2,4-D	24	1.5	0.15	48.2	-0.0009
2,4-D	24	1.5	0.15	29.6	-0.00005

Table 4.13. Fenox concentration from the batch experiments after 8h

Pesticide	Time (hr)	Mass of soil (g)	Batch test volume (L)	Initial conc. (µg L^{-1})	Sorbed conc. (mg g^{-1})
Fenox	8	1.5	0.15	34.3	0.0014
Fenox	8	1.5	0.15	16.6	0.0008
Fenox	8	1.5	0.15	8.3	0.0004
Fenox	8	1.5	0.15	2.9	0.0002
Fenox	8	1.5	0.15	1.3	0.0001

Table 4.14. Fenox concentration from the batch experiments after 24h

Pesticide	Time (hr)	Mass of soil (g)	Batch test volume (L)	Initial conc. (µg L^{-1})	Sorbed conc. (mg g^{-1})
Fenox	24	1.5	0.15	34.3	0.0025
Fenox	24	1.5	0.15	16.6	0.0014
Fenox	24	1.5	0.15	8.3	0.0007
Fenox	24	1.5	0.15	2.9	0.0003
Fenox	24	1.5	0.15	1.3	0.0001

As a final step for the investigation of sorption behavior, equilibrium sorption isotherms were constructed for both herbicides and for the hours 8 and 24. It can be clearly seen from the Figure 4.10, that no clear relation between the aqueous and sorbed concentrations attributed to the low sorption potential of 2,4-D. The experiment can give a very limited idea on the sorption behavior of 2,4-D. Some researchers studied 2,4-D sorption with five different soil samples. One of these soil samples had a similar characteristic with the soil that is used in this batch experiments. The optimum soil/solution ratio was selected as 1:5 and 2,4-D concentrations in the aqueous phase was determined by UV-VIS spectrometer. The prepared concentrations were between 0-100 mg L^{-1}. An increasing trend in the adsorbed content was observed mostly after 12 h equilibration (Bekbölet et al., 1999). An efficient sorption in this study may not be achieved since lower concentrations were studied and the

soil/solution ratio was much higher when it is compared to the prementioned study. Table 4.15 indicates the K_d values obtained from other studies on the 2,4-D sorption potential. The low sorption potential of 2,4-D obtained in this study with the soil samples obtained from the Konya Plain are consistent with the data from the literature.

Table 4.15. Summary of some K_d values obtained from the literature

Sorbent	**Region**	**K_d (L kg^{-1})**	**Isotherm**	**Analytical method**	**Reference**
Calcerous and terra rosa soil	Antalya, Turkey	0.95	Linear	UV-VIS	(Gurson et al., 2019)
Natural soil	Turkey	0.321-1.89	Linear	UV-VIS	(Bekbölet et al., 1999)
Soil	-	0.16	Freundlich	-	(Werner et al., 2013)
Soil	France, Brazil, New Caledonia	0.3-9.5	-	Liquid scintillation counting	(Dubus et al., 2001)
Urban soil	Newcastle, Australia	0.65-4.68	Linear, Freundlich, Langmuir	LC-MS	(Meftaul et al., 2020)

"-", no data available

On the other hand, the linear regression coefficients (R^2) for Fenox equilibrium sorption isotherms were between 0.973 and 0.968 (Figure 4.11) which suggests that the Fenox sorption follows a linear isotherm. Furthermore, Figure 4.11 indicates that the K_d of the Fenox at the hours 8 and 24 are 75.6 mL g^{-1} and 297.4 mL g^{-1} respectively. 24th hour K_d is correlated with the data from the International Union of Pure and Applied Chemistry (IUPAC) database (IUPAC, 2022).

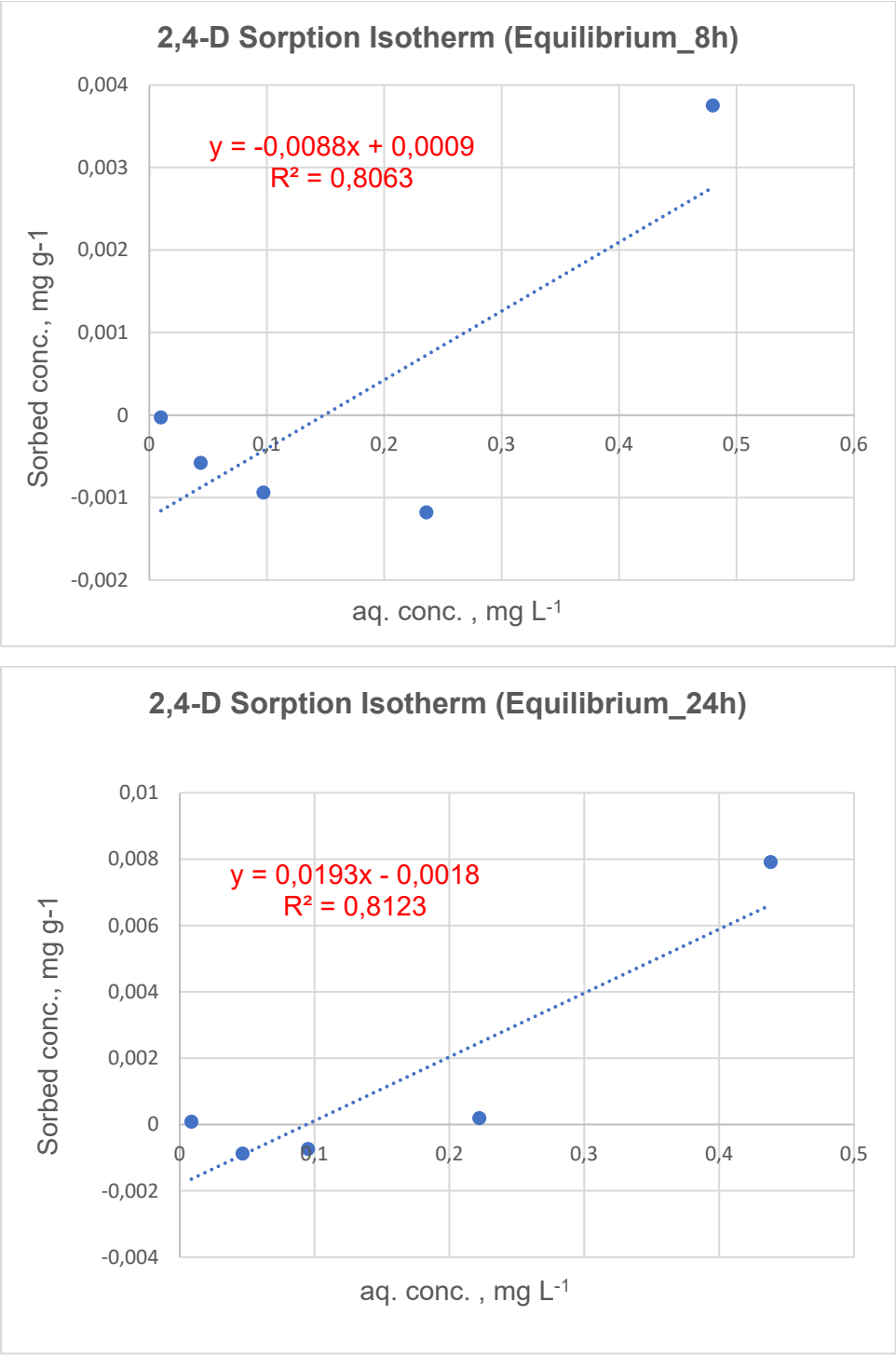


Figure 4.10. Sorption isotherms of 2,4-D for the hours 8 and 24 respectively

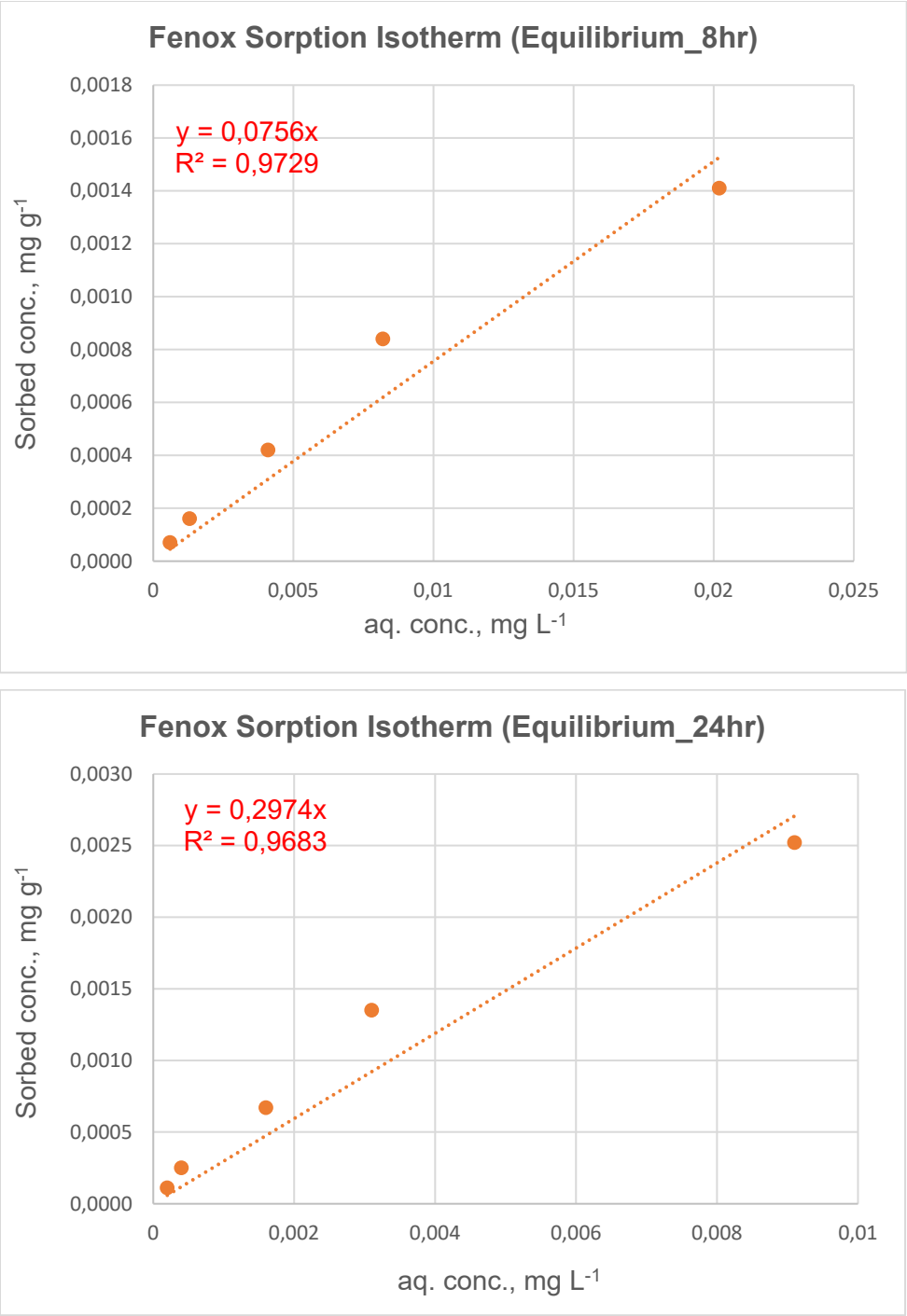
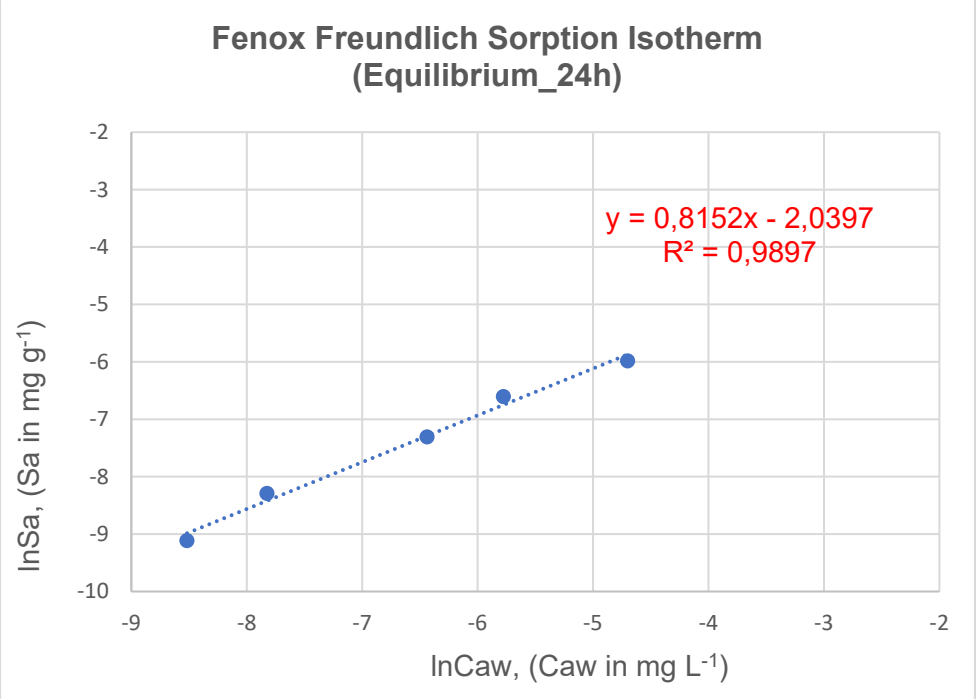


Figure 4.11. Sorption isotherms of Fenox for the hours 8 and 24 respectively

In addition to the linear sorption isotherms, Freundlich and Langmuir isotherms were also constructed for Fenox and for the 24th hour (Figure 4.12).



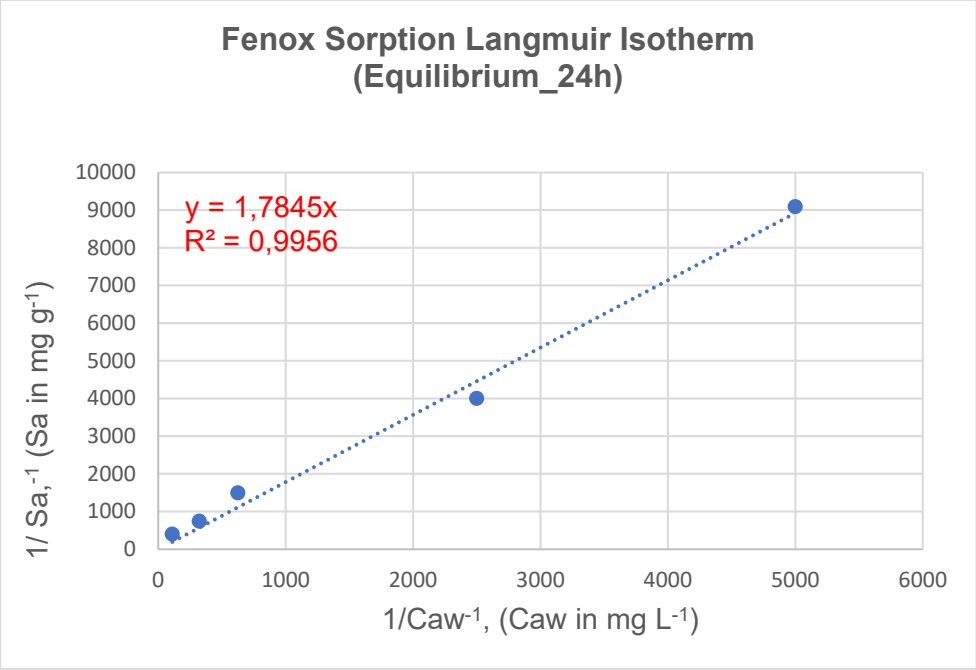


Figure 4.12. Freundlich and Langmuir sorption isotherms for Fenox for data after 24th hour

4.5. Column Transport Experiments

4.5.1. 0.01 M NaCl Tracer Test for 2,4-D experimental set-up

In order to establish the dispersion properties of the column that is used for the transport experiments, 0.01 M NaCl tracer test was performed prior to the pesticide transport experiments.

Because a tracer undergoes no sorption, the only transport mechanisms are advection and dispersion. The column was filled with 30 g of soil/sand (3:7, w/w) mixture. The pore volume of the column was estimated to be 8 mL. The first change in the EC was measured at the 16th min for the flow rate of 0.75 mL min^{-1} and it was 17th min for the flow rate of 1.00 mL min^{-1} (Table 4.15).

Table 4.15. 0.01 M NaCl tracer test results for 2,4-D column experiment

Sample#	Sample (mL)	Time (min) Q= 0.75 mL min^{-1}	Time (min) Q= 1.00 mL min^{-1}	EC (µS cm^{-1}) Q=0.75 mL min^{-1}	EC (µS cm^{-1}) Q= 1.00 mL min^{-1}
1	1	1.4	1.2	0	0
2	1	2.8	2.4	3.7	3.7
3	1	4.2	3.6	0.2	-0.7
4	1	5.6	4.8	-3	-3.8
5	1	7	6	0.6	5.8
6	1	8.4	7.2	21.7	21.8
7	1	9.8	8.4	52.1	36.5
8	1	11.2	9.6	71.8	51.7
9	1	12.6	10.8	82.9	62.8
10	1	14	12	92.2	68.8
11	1	15.4	13.2	96.1	78.8
12	1	16.8	14.4	98.1	82.6
13	1	18.2	15.6	98.7	84.6
14	1	19.6	16.8	98.4	82.5
15	1	21	18	99.8	88.8
16	1	22.4	19.2	101.8	91.7
17	1	23.8	20.4	103.4	93.2
18	1	25.2	21.6	99.5	96.1
19	1	26.6	22.8	100.3	89.2
20	1	28	24	98.8	88.2
21	1	33.6	28.8	98.2	89.9
22	1	39.2	33.6	99.2	103.7
23	1	44.8	38.4	98.7	94.6
24	1	50.4	43.2	99.3	92.1

By adjusting the parameters such as flow rate, and porosity on a model, dispersion coefficients of different flow rates were calculated. The dispersion coefficients for the flow rates of 0.75 mL min^{-1} and 1.00 mL min^{-1} were calculated as 3.25 cm^2 min^{-1} and 7.30 cm^2 min^{-1} respectively. Figure 4.13 indicates that the EC for the flow rates of 0.75 mL min^{-1} and 1.00 mL min^{-1} were approximated as 98 µs cm^{-1} and 92 µs cm^{-1}. Equation 4.3 is used for the modelling of the tracer (Bedient et al., 1999).

$$C = \frac{C_o}{2} erfc\left[\left(\frac{x - Vt}{D}\right) + e^{VX/D} erfc\left(\frac{x + Vt}{D}\right)\right] \quad (4.3)$$

Where, x is the length of the column (cm), V is the velocity (cm min^{-1}), t is the time (min) and D is the dispersion coefficient (cm^2 min^{-1}). and *erfc*() is the compliment of the error function.

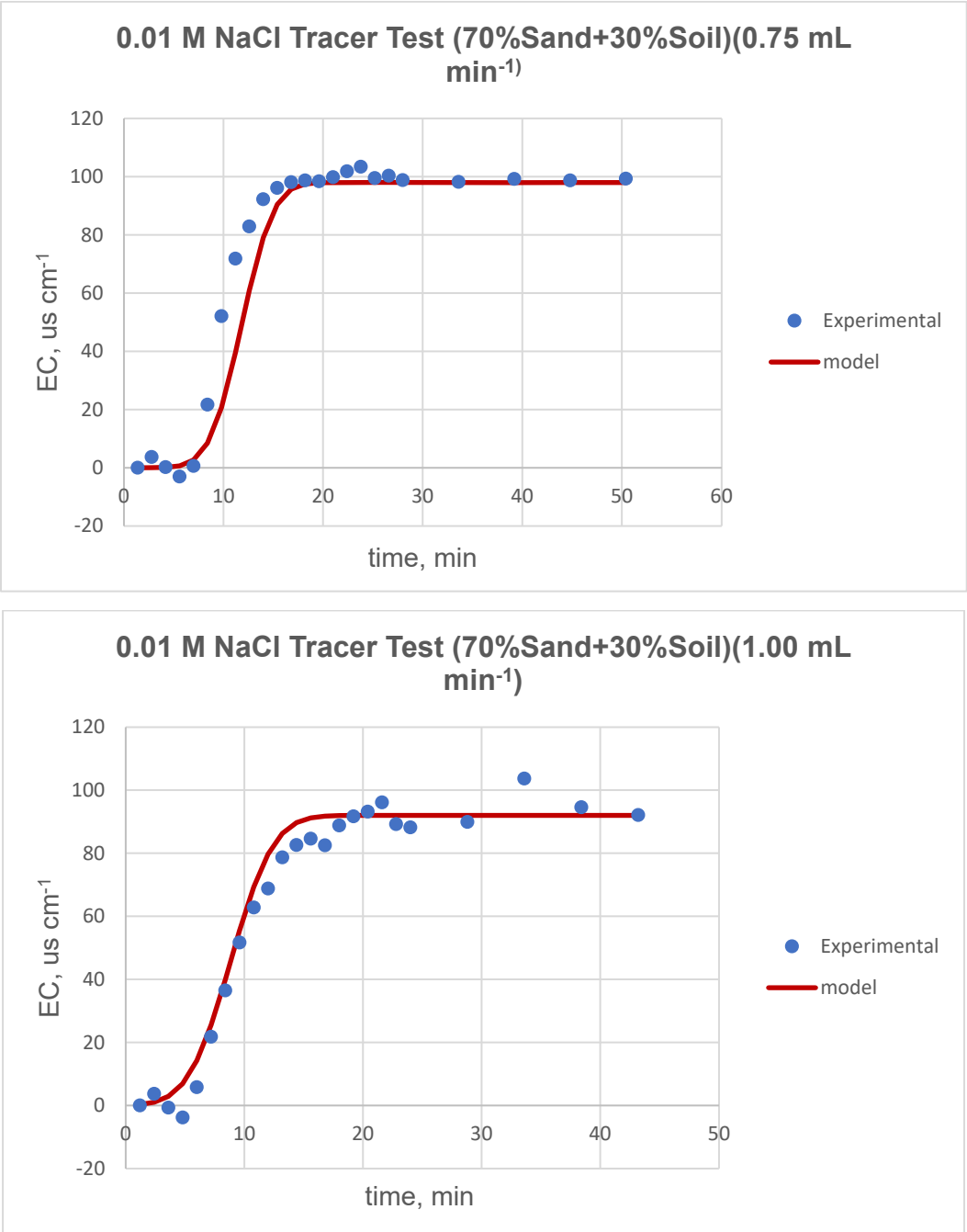


Figure 4.13. Comparison between the experimental breakthrough curve for 2,4-D and the data from the model

Figure 4.14 shows that the combination of both experiments for the two different flow rates. It can be seen that the retention time at a higher flow rate is shorter which means the transport of a contaminant through the soil reaches the effluent point faster with the higher flow rates. Moreover, the dispersivity of the two experiments are close to each other: 3.2 cm and 5.4 cm. It is reported in the literature that the dispersivity is function of the heterogeneity of the soil and the travel distance (Gelhar, 1993). The dispersivity is not a parameter that can be measured directly but is typically determined indirectly from tracer tests such as the ones conducted in this study. Typical values of are a fraction of the total length of the column, between 5% and 20% depending on the degree of soil heterogeneity. The values obtained in this experiment are consistent with the range of values reported in the literature.

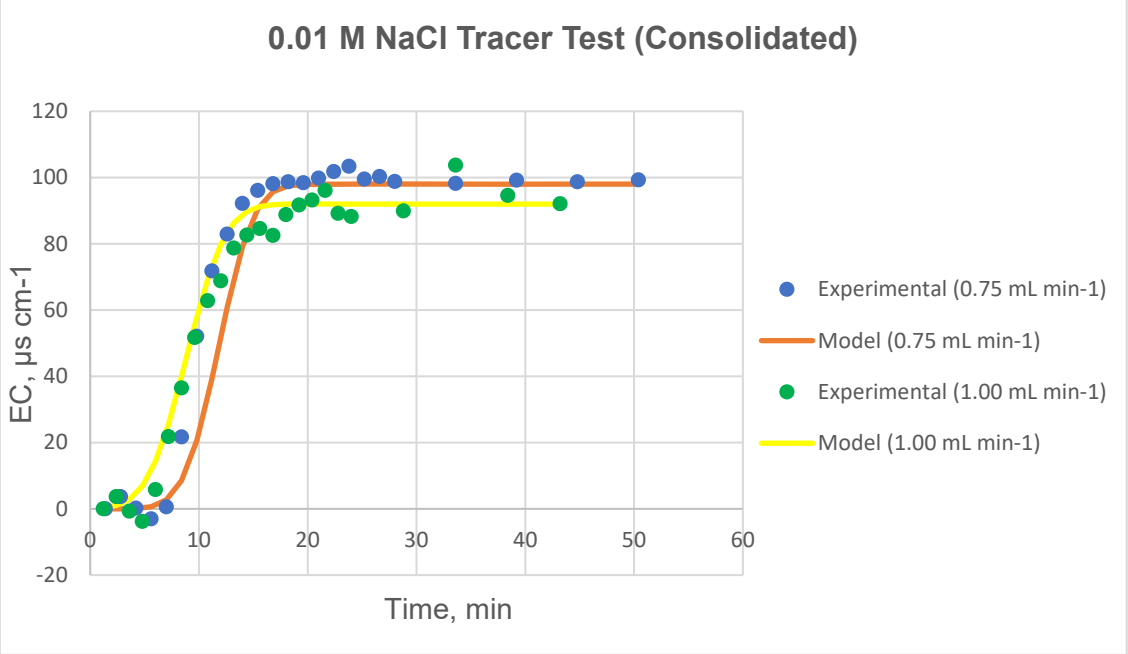


Figure 4.14. Tracer breakthrough curves for the two different flow rates

4.5.2. 0.01 M NaCl Tracer Test for Fenox experimental set-up

Since another packing method of soil to the column was applied, an additional tracer test for the column transport experiment of Fenox. The column was filled with 20 g of soil/sand (3:7, w/w) mixture. The flow rate was set to be 1.00 mL min^{-1}. The first change in the EC was measured at the 35^{th} min for the flow rate of 1.00 mL min^{-1} (Table 4.16).

Table 4.16. 0.01 M NaCl tracer test results for Fenox column experiment

Sample#	Sample (mL)	Time (min)	EC (µS cm^{-1})
1	1	0	0
2	1	5	0.87
3	1	10	1.08
4	1	15	4.56
5	1	20	8.17
6	1	25	12.87
7	1	30	14
8	1	35	17.89
9	1	40	20.09
10	1	45	23.29
11	1	50	23.39
12	1	55	20.89
13	1	60	21.29
14	1	65	19.99
15	1	70	20.49
16	1	75	21.29
17	1	80	20.99
18	1	85	21.79
19	1	90	22.09
20	1	95	23.79

The dispersion coefficient was calculated as 44.74 $cm^2\ min^{-1}$. Figure 4.15 indicates that the EC and the mean arrival time for the 0.01 M tracer test was approximated as 22 µs cm^{-1} and 40 min, respectively. It can be seen that the model and the experiment fit well.

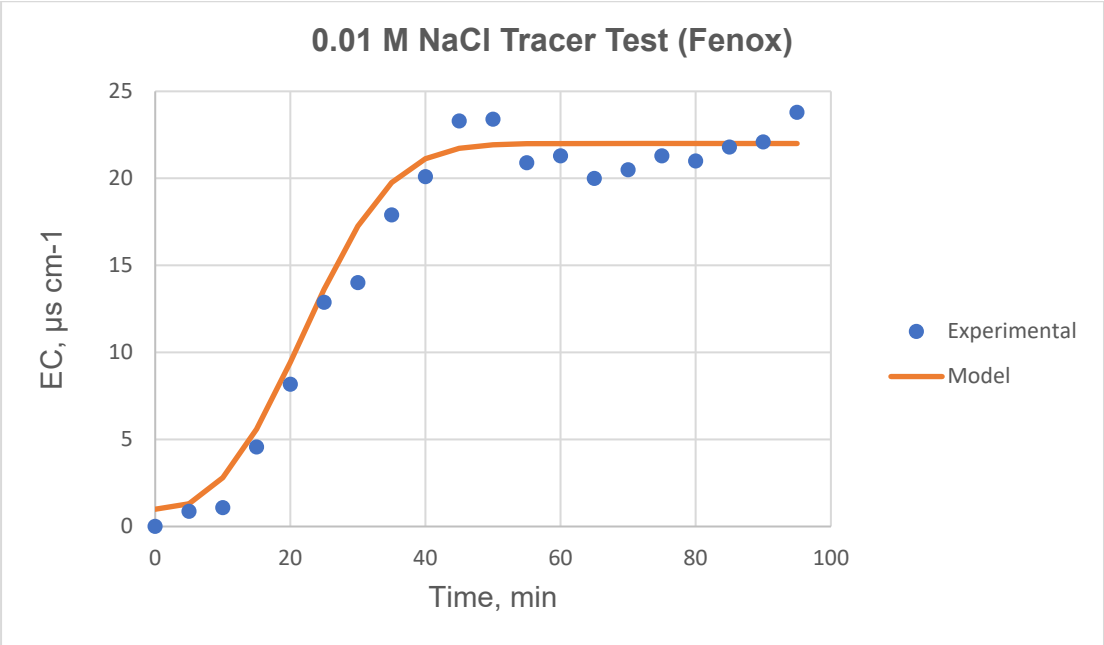


Figure 4.15. Comparison between the experimental data for Fenox and the data from the model

4.5.3. 2,4-D Column Experiment

Concentration of a 500 µg L^{-1} 2,4-D working solution was prepared for the column transport experiments of 2,4-D. The dispersion coefficient of the experiment was calculated as 7.71 cm^2 min^{-1} and breakthrough time was calculated as roughly 21 min (Figure 4.16). The retardation factor used to fit the data with the model was indicating that 2,4-D undergoes little sorption. This suggests that 2,4-D is quite mobile and therefore causes more risk of migration to the groundwater or nearby surface water bodies.

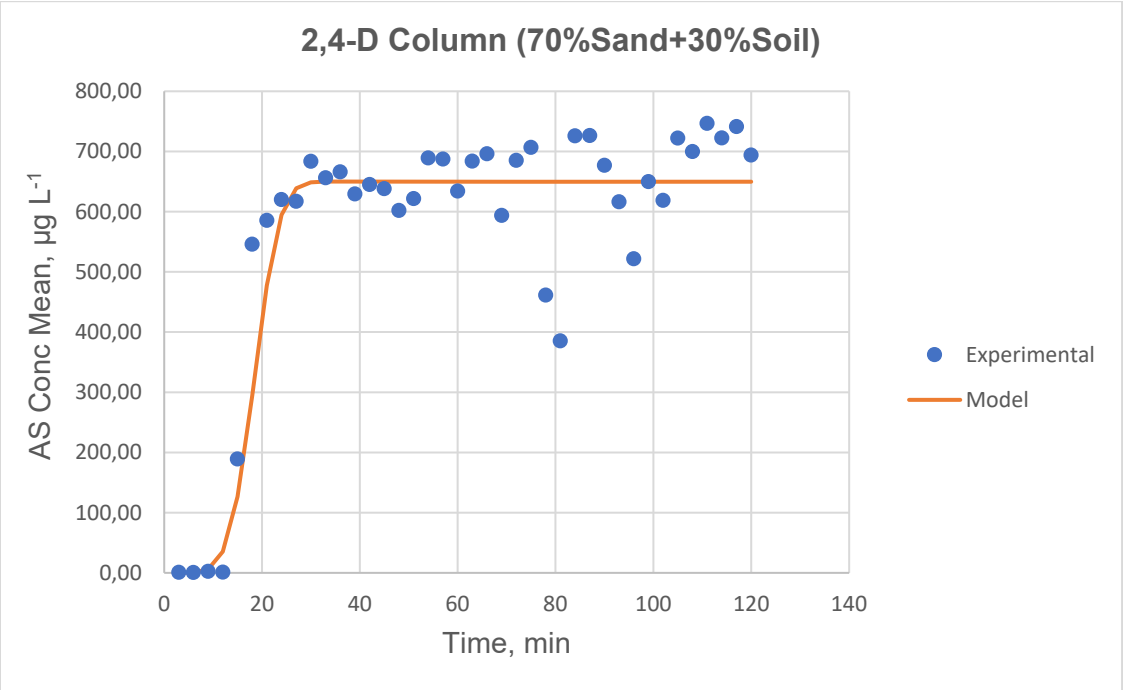


Figure 4.16. Breakthrough curve of 2,4-D

4.5.4. Fenox Column Experiment

Concentration of a 500 µg L^{-1} Fenox working solution was prepared for the column transport experiments of Fenox. The dispersion coefficient of the experiment was calculated as 44.74 cm^2 min^{-1} and breakthrough time was estimated form the model as roughly 250 hours (Figure 4.17).

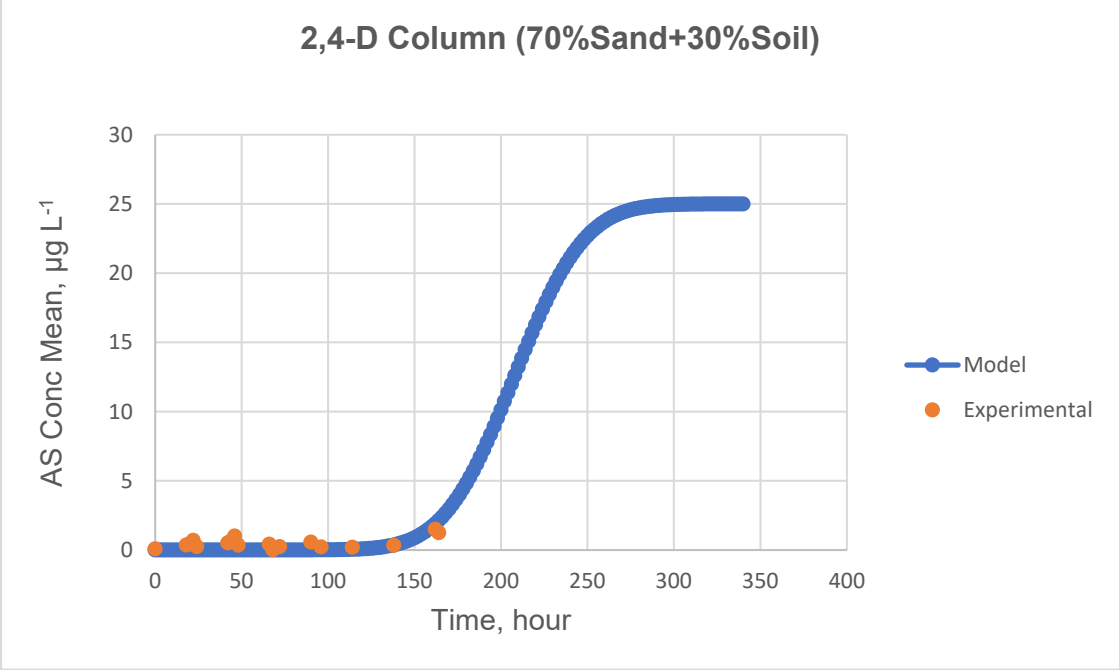


Figure 4.17. Breakthrough curve of Fenox

Since the duration of the experiment was relatively short, this equation provides a rough approximation of the breakthrough curve. The breakthrough time was estimated as 250 hours.

5. CONCLUSIONS

This laboratory scale study aimed to investigate the fate and transport behavior of some commonly used pesticides in the Konya Plain. With this regard, 2,4-D and Fenox were selected as the target since they are widely used in the farmlands of the Konya Plain. Using real soil samples, batch and column experiments were performed. A state-of-the-art measurment technique using LC-MS/MS was employed in the experimental work for the detection of the selected chemicals during the experiments. Although there are variety of studies conducted on the sorption behaviour of 2,4-D available in literature, as far as encountered, there is very limited data available for Fenox. While this lack of information made the literature survey and discussion of the results obtained relatively difficult, on the other hand, it also added originality and novelty to the study conducted as well. It must be taken into account that, determination of fate and behaviour of the most commonly used chemicals applied to the soil for different purposes, is of great importance in order to assess the potential impacts of these chemicals on the environment and eventually human health.

In this work, after the characterization of the soil samples, it was aimed to investigate the pesticide contamination in the soil samples by using QuEChERS method. It was necceserray to obtain a water content below 6% for all of the samples. Firstly, a commercial plant was spiked with 1µg of each surrogate standard and herbicide, then extraction was achieved with both AOAC and BS methods. The extracts were analyzed using the LC-MS settings given above with the sMRM parameters optimized for each chemical substance. The mean recovery of surrogate standards and target herbicides from the soil by AOAC and BS methods were found to be 45.4±14.1 and 51.6±28.2% (*n=21*), respectively. No significant difference was observed between the recovery efficiencies of the two methods. Since there is a lower need of chemical consumption and it has been preferred in screening the pesticide contamination in European soil, the AOAC method was selected as a pesticide extraction method for the soil samples that was collected for this study. Moreover, recovery results suggest that the target herbicides have tendency to sorb on soil but their sorption extent can accurately be interpreted by using the selected surrogate standards. As a result, in order to calculate the concentrations of positively and negatively ionized herbicide residues in soil, Pos1 and Neg1 were selected, respectively, since they have similar recovery efficiencies with target herbicides in AOAC method. The extracts obtained by AOAC QuEChERS method were analyzed by both targeted and non-targeted LC-MS methods. None of the target herbicides was detected over the LOD in the extracts.

Dinoterb, vamidothion and azoxystrobin were detected in almost all of the samples. Dinoterb is nitrophenolic herbicide which was banned in EU since it is persistent in the environment. It is estimated that the residues were belong to previous field applications as they are persistent pollutants in the environment. Although it was banned in the EU, vamidothion, an organic thiophosphate insecticide, still seems to be used to control the insects in Turkey. Moreover, azoxystrobin, which is a broad-spectrum fungicide, was detected at very high concentrations in the soil samples. It might be due to frequent application of this pesticide in the fields. In addition, 2,4-D and 4-CPA, which is a homolog of 2,4-D, was detected in the soil samples taken from pivot-2 and 7 where wheat is planted. Although, 4-CPA and 2,4-D are not used in those fields, probably they formed via biotransformation of 2,4-D 2-ethylhexyl ester used in the fields. The samples taken particularly from Pivot-13, which has not been planted for some time, had very characteristic pesticide profile. Samples 16 and 17 have fenpropimorph, epoxiconazole, propiconazole and difenoconazole. These fungicides are commonly used in the protection of cereal crops.

After the soil characteristics determination of the soil samples to be used for batch sorption tests and column experiments and the pesticide residue monitoring, batch sorption tests were conducted for 2,4-D and Fenox, respectively. The objective of these batch sorption tests were to examine the sorption kinetics and to determine K_d values for the isotherm constant 2,4-D and Fenox. Determination of the K_d value has a great importance in the understanding of adsorption/retardation factors of the target contaminants. As a result of batch sorption experiments, there was no significant K_d value calculated. On the other hand, Fenox sorption was achieved after 24 hour equilibration. The K_d value for Fenox was calculated as 297.4 mL g^{-1} based on the 24^{th} hours data. The K_d value of 2,4-D is quite lower than Fenox and this might be the reason that no sorption was achieved during the batch sorption tests. The high sorption potential of Fenox observed from the batch sorption tests show that this pesticide has a very low leaching potential compared to 2,4-D. It means that Fenox has a higher tendency to accumulate in soil and plants. On the other hand, 2,4-D poses a greater risk for the contamination of groundwater and nearby surface water resources.

After the batch sorption tests were completed, column experiments were performed for 2,4 D and Fenox, respectively. The objective of the column experiments were to determine the transport behavior of both chemicals in the soil samples under pre-determined parameters and laboratory conditions. Before conducting the column trasport experiments with the target pesticides, a non-reactive tracer test was applied. For the 2,4-D experimental set-up, 0.01 M NaCl tracer test was resulted with the first changes in ECs as 16^{th} and the 17^{th} min. for the flow rates 0.75 mL min^{-1} and

1.00 mL min^{-1}, respectively. Also for the same flow rates, the dispersion coefficients were calculated as 3.25 $cm^2 min^{-1}$ and 7.30 $cm^2 min^{-1}$ respectively. After the tracer test, 2,4-D was applied as a solution with a concentration of 500 µg L^{-1} at a 1.00 mL min^{-1} flow rate. The breakthrough time and the dispersion coefficient for 2,4-D were determined as 21 min. and 7.71 $cm^2 min^{-1}$ respectively. These results correlates the data with the findings from the batch sorption tests. It can be assumed that again no sorption was achieved during the column experiments. The retention time and the dispersion coefficient values were found to be very similar to the tracer test at the same flow rate. For the Fenox experimental set-up, 0.01 M NaCl tracer test was also applied. The first change in the EC was observed at the 35^{th} min. for the flow rate 1.00 mL min^{-1}. The disersion coefficient was calculated as 44.74 $cm^2 min^{-1}$. After the 0.01M NaCl tracer test, a concentration of 500 µg L^{-1} Fenox solution was applied at a 1.00 mL min^{-1} flow rate. Since the duration of the colum experiment was not sufficient because of the high level of sorption of FENOX, the data only provides an approximation of the breakthrough curve using the 1D transport equation.The breakthrogh time was estimated as rougly 250 hours with a dispersion coefficient 44.74 $cm^2 min^{-1}$.

In the light of the results that were obtained from this study, it can be concluded that the Fenox has a much higher sorption capacity in comparison to 2,4-D. Therefore, 2,4-D has a greater potential to reach the other environmental systems.

For future research, it can be suggested to investigate that the possible biotransformation products of 2,4-D since its high mobility due to leaching potential. In addition, mathemathical models can be developed in order to estimate the possible transport routes of 2,4-D. Another suggestion is to examine the sorption behavior for different organic content in the soil. Use of the samples with different organic contents will help to improve our understanding of sorption behavior of the pesticides for different field conditions. At last but not least, it was obtained a highly significant K_d value for the Fenox, which is a success of this study when taking into account that there was very limited data on Fenox sorption behaviour. Future research can focus on conducting a more comprehensive study on the fate and transport of Fenox in the environment.

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